Harding Lawson Associates

September 29, 1997

37933 004

Mr. Wayne Praskins
Superfund Remedial Project Manager
U.S. EPA Region IX
75 Hawthorne Street
San Francisco, California 94105-3901

Transmittal of Technology Screening
for the Treatability of Perchlorate in Groundwater
Baldwin Park Operate Unit (BPOU), San Gabriel Basin

Dear Mr. Praskins:

Please find enclosed a copy of *Technology Screening for the Treatability of Perchlorate in Groundwater,*
Baldwin Park Operable Unit, San Gabriel Basin, dated September 29, 1997. This Technology
Screening Report was prepared by Harding Lawson Associates and is submitted on behalf of the
BPOU Steering Committee.

Should you have any questions regarding this document, please contact either Don Vanderkar at (916)
355-4282 or me at (415) 899-8825.

Yours very truly,

HARDING LAWSON ASSOCIATES

John G. Catts, Ph.D.
Chief Technical Officer

JC/hk
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Enclosure

cc: Mr. David Towell - CH2M Hill

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DRAFT
Technology Screening for the
Treatability of Perchlorate In Groundwater
Baldwin Park Operable Unit
San Gabriel Basin

Prepared for

Baldwin Park Operable Unit Steering Committee

HLA Project No. 37933 004

September 29, 1997

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DRAFT
Technology Screening for the Treatability of Perchlorate In Groundwater Baldwin Park Operable Unit San Gabriel Basin

Prepared for

Baldwin Park Operable Unit Steering Committee

HLA Project No. 37933 004

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Vice President

September 29, 1997

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1.0 INTRODUCTION

For the past several years, the Baldwin Park Operable Unit Steering Committee (BPOUSC), the U.S. Environmental Protection Agency (EPA) Region IX, the Three Valleys Municipal Water District (TVMWD), and the Metropolitan Water District of Southern California (MWD) have been planning a combined groundwater remediation and water supply project in the San Gabriel Basin. Project planning was initiated in response to a requirement of EPA to remediate a plume of volatile organic compounds (VOCs) in groundwater distributed from locations north of Interstate 210 in the city of Azusa southwest to locations in the vicinity of Interstate 10 in the city of Baldwin Park. This area is called the Baldwin Park Operable Unit (BPOU).

1.1 General Background

The BPOUSC was in the process of negotiating agreements with EPA, MWD, and TVMWD to extract VOC-impacted groundwater, treat this water to remove VOCs, and deliver the water to TVMWD via a wheeling agreement with MWD, when in June 1997, concentrations of perchlorate ion above the State of California Department of Health Services (DHS) provisional action level of 18 micrograms per liter (μg/L) were found in groundwater within the BPOU and other portions of the San Gabriel Basin. Additionally, perchlorate has recently been detected in groundwater at other facilities in California, Nevada, and Utah.

Before the project can progress, perchlorate's potential impact on the conceptual project design must be evaluated. The presence of perchlorate in BPOU groundwater is particularly troublesome for several reasons. First, insufficient information is known about the long-term effects of low concentrations of perchlorate on human health. Therefore, based on evaluations by EPA and DHS, a very conservative "provisional" action level with a 300-fold margin of safety has been established. As appropriate toxicological studies are completed, this action level could change significantly.

Second, there is no treatment technology that has been demonstrated to be effective in reducing concentrations of perchlorate ion in water to a concentration below the DHS provisional action level. Pilot-scale treatability testing of a biochemical reduction technology has been successfully performed at the Aerojet General Corporation (Aerojet) site in Sacramento. However, the pilot test at this site was conducted at a flow rate equivalent to 4 percent of the design flow at the BPOU, the influent perchlorate concentration was over 100 times that expected in the BPOU, and the pilot system was not designed to achieve nor did it achieve effluent perchlorate concentrations less than the 18 μg/L provisional action level.

Third, the EPA Record of Decision (ROD) for the BPOU was issued in 1994, long before the discovery of perchlorate in BPOU groundwater and the establishment of the 18 μg/L provisional action level by DHS. Consequently, the current remedy proposed for the BPOU, specifically the groundwater extraction and treatment system, does not address perchlorate as a chemical of concern. In addition, the ROD does not address delivery or recharge of treated water with concentrations of perchlorate above the DHS provisional action level.

1.2   Site Description and Background

Perchlorate was first detected in San Gabriel Basin groundwater in late June 1997 by DHS. This prompted the Main San Gabriel Basin Watermaster (MSGBWM) and the BPOUSC to perform additional groundwater sampling and analysis to better understand the distribution of perchlorate in groundwater.

To date, the BPOUSC has compiled perchlorate data from over 50 monitoring wells, production wells, and sampling points in the vicinity of the BPOU. Perchlorate analysis for production wells was performed on samples obtained by DHS and MSGBWM and provided by the San Gabriel Basin Water Quality Authority (SGBWQA). Groundwater samples from monitoring wells in the BPOU were collected by Camp Dresser & McKee (CDM), Harding Lawson Associates (HLA), and Geosyntec on behalf of the BPOU. All available data on perchlorate concentrations in groundwater in the San Gabriel Basin were provided in a report prepared by HLA dated July 1997 (HLA, 1997a).

Based on these initial data, the approximate lateral distribution of perchlorate in groundwater at concentrations greater than the DHS provisional action level of 18 μg/L was estimated and is illustrated on Figure 1-1. This approximate perchlorate distribution is based on maximum concentrations detected in any sample or at any depth within a given well. Maximum concentrations are posted next to each well location. Similarly, the approximate vertical distribution of perchlorate in groundwater was estimated and is illustrated on the cross section shown as Figure 1-2. This cross section is oriented along the generalized direction of groundwater flow within the BPOU as shown on Figure 1-1. Based on the distribution of perchlorate in groundwater described in the July 1997 HLA report (HLA, 1997a), it has been estimated that groundwater extracted by the proposed project will contain approximately 50 to 100 μg/L of perchlorate.

It should be noted that for the majority of the wells sampled, only a single sample has been collected. Further, the extent of perchlorate both upgradient and downgradient of the BPOU has not been fully defined, and areas beyond the immediate boundaries of VOCs detected in the BPOU have not been

sampled. Therefore, the known distribution may change as wells are resampled or new wells are sampled.

The BPOUSC is currently installing additional monitoring wells to better define the extent of concentrations of perchlorate above the DHS provisional action level. This work is described in a document entitled "Addendum to Sampling and Analyses Plan" (HLA, 1997b). When these wells are installed, a second comprehensive round of sampling, including both monitoring and production wells, will be performed.

Perchlorate found in San Gabriel Basin groundwater could have originated from one or more sources. Potassium perchlorate is a compound commonly used in fireworks, explosives, and flares. Perchloric acid is commonly used in metal etching and cleaning operations. Ammonium perchlorate is a component of solid rocket fuel. Based on a preliminary records review, perchloric acid, potassium perchlorate, and ammonium perchlorate were all used and disposed within the BPOU. A common and approved disposal practice for perchlorate salts is burning. Both ammonium and potassium perchlorate are highly soluble salts that readily dissolve in water. Once dissolved, the perchlorate remains in solution, Because of its stable ionic characteristics (low charge density). The perchlorate ion is not readily degraded, retarded, or precipitated and therefore is a conservative solute in water, migrating at the same rate as groundwater.

1.3   Planned BPOU Project

To achieve multiple objectives, the current project combines groundwater remediation, water supply, and conjunctive use. This project is designed to extract groundwater contaminated with VOCs in two areas, treat the extracted water, and deliver the treated water to water supply systems. Pumping would occur at a fairly consistent rate throughout most of the year. System throughput is estimated to be approximately 20,000 gallons per minute (gpm).

As the BPOUSC has no water rights in the basin, the volume of water extracted will need to be recharged. Recharge may occur during a portion of the year, or it may be postponed from one year to the next depending upon water levels in the basin or the availability of water for recharge. Therefore, the project has a conjunctive use component and affords drought protection for those receiving the treated water.

Because of the presence of VOCs in groundwater and the complexities that the presence of such organic compounds imparts on a variety of potential perchlorate treatment technologies, the extracted groundwater will first be treated to remove VOCs using air stripping with a vapor-phase granular activated carbon (GAC) emission control system. Upon removal of VOCs, the effluent, still containing up to 100

μg/L of perchlorate, will then be processed through the selected treatment technology for removal of perchlorate. The goal is to render the water potable. Based on current standards, "potable" is considered to be water containing concentrations of perchlorate less than the 18 μg/L DHS provisional action level. If possible, water will be treated to levels less than the current laboratory reporting limit of 4 μg/L.

Based on historical sampling and analysis of groundwater in the BPOU and the proposed plan for extraction of groundwater, it has been estimated that the extracted groundwater will contain between 15 and 25 milligrams per liter (mg/L) of nitrate (as NO_3). Although this concentration is well below the state and federal Maximum Contaminant Level (MCL) of 45 mg/L, this concentration is higher than that present in waters some local and regional water purveyors provide to their customers. Pilot-scale studies performed in 1995 and 1996 by Aerojet in Sacramento confirmed that the nitrate and perchlorate ions are chemically similar and are both amenable to treatment by biochemical reduction. Therefore, it is a second goal of the BPOUSC to secure a treatment technology that will reduce concentrations of nitrate.

For the purposes of this study, it was assumed that treatment of perchlorate and nitrate will take place subsequent to the removal of VOCs and will be an independent process from the planned air stripping. Although the concept of pretreating the extracted groundwater stream for perchlorate prior to VOC treatment has not been completely discounted, and modifications to the treatment train are under consideration, this study focuses on treatment of perchlorate only and assumes the influent stream will be relatively free of organic constituents.

1.4   Purpose of Study

The purpose of this study is to perform a thorough evaluation of all treatment technologies, other than biochemical reduction, that have potential for removing perchlorate, and if possible nitrate, from extracted groundwater. Specifically, this evaluation:

- Performs a technical feasibility evaluation on these specific treatment technologies considering applicability of treatment for perchlorate, effectiveness of perchlorate removal, and technical difficulty associated with implementation of the technology.

- Examines a wide range of different technologies with potential for treating perchlorate (or other anions with similar physical properties) in groundwater. These include physical, chemical, and biological technologies with particular focus on physical and chemical technologies.

- Identifies several specific treatment processes with the greatest potential to successfully meet treatment objectives.

- Conducts a comparative cost analysis of these treatment technologies to aid in determination of the overall feasibility of candidate treatment alternatives.

- Provides recommendations for further bench-scale and/or pilot-scale testing of promising technologies.

1.5   Biological Treatability Testing

In response to the detection of perchlorate in groundwater beneath its 8,000-acre facility near Sacramento, California, Aerojet began evaluating and testing technologies for the removal of perchlorate from groundwater in 1994. This work consisted of a technology screening, laboratory bench-scale studies, and pilot-scale studies. Although several technologies were examined and tested (biochemical reduction, ion exchange, electrodialysis, and chemical reduction), biochemical reduction proven to be the most efficient and cost effective of the technologies examined.

The biochemical reduction process was proven to be effective at reducing perchlorate concentrations in extracted groundwater from approximately 7,000 to 8,000 μg/L to below the laboratory detection limit (400 μg/L). Concentrations of nitrate were reduced from approximately 1.5 mg/L to less than 0.5 mg/L. The process employs a fixed film biorector where the fixed film is attached to granular activated carbon operated as a fluidized bed (GAC/FB).

As part of the BPOU project, additional pilot-scale testing of this technology is in progress. The purpose of this additional testing is to establish if effluent perchlorate concentrations, less than the 18 μg/L provisional action level, are achievable. Phase 1 of this treatability testing is underway at Aerojet's Sacramento facility and is described in more detail in a document entitled "Phase 1—Treatability Study Work Plan" (HLA, 1997c). In addition, Aerojet has just passed the 60 percent design stage for the implementation of a full-scale biochemical reduction system using the GAC/FB technology, with a design capacity of 1500 gpm, to remove perchlorate from groundwater at one of several Sacramento Groundwater Extraction and Treatment (GET) systems. Although this technology is not being evaluated in this study, a detailed technology scoring and an engineering cost estimate are provided for comparison with alternative treatment technologies in Section 6.0.

1.6   Report Organization

This report is organized as follows:

Section 1.0   Introduction - Background and general site information is provided in this section.

Section 2.0   Objectives and Methodologies - The objectives of this feasibility evaluation for perchlorate treatment technologies are discussed. Additionally, the methodologies used to research treatment technologies are discussed.

Section 3.0   Physical and Chemical Properties of Perchlorate - Physical and chemical properties of perchlorate are discussed to better understand the applicability and potential effectiveness of the treatment technologies evaluated.

Section 4.0   Identification of Candidate Technologies - The physical and chemical treatment technologies applicable for treatment of perchlorate in extracted groundwater are discussed.

Section 5.0   Initial Technology Screening - An evaluation of the treatment technologies described in Section 4.0 is presented. The evaluation includes consideration of effectiveness of technology, implementability, cost, and acceptance.

Section 6.0   Conceptual Design and Cost Evaluation - A conceptual design and cost evaluation is presented for each of the technologies that passed the screening evaluation described in Section 4.0.

Section 7.0   Recommendations and Proposed Activities - Based on the outcome of the overall technical feasibility screening, selected treatment technologies are proposed for further testing.

2.0 OBJECTIVES AND METHODOLOGY

The purpose of this section is to describe the specific objectives of this identification and screening of perchlorate treatment technologies.

2.1 Objectives

The goal of this study is to evaluate a full range of technologies for potential application to perchlorate treatment and recommend a treatment technology or technologies for bench-scale and/or pilot-scale testing that have the potential to generate an end product (treated groundwater) that is potable.

The DHS provisional action level for perchlorate is 18 μg/L, i.e., the level at which it is recommended that utilities inform their customers of the presence of perchlorate in supply water. The objective of this study is to recommend a treatment technology(ies) that can meet or exceed a treatment goal of 18 μg/L; however, it is possible that discharge standards for perchlorate may be lower than 18 μg/L. Therefore, it is this study's goal to recommend a treatment technology(ies) that has strong potential to treat groundwater to below the DHS provisional action level and preferably to nondetectable (currently 4 μg/L) concentrations.

The current design flow rate for the BPOU project is approximately 20,000 gpm. Testing of biological treatment methods (by HLA and others) has shown these methods to be effective in reducing perchlorate and nitrate concentrations in water. Pilot-scale testing of a biochemical reduction technology is in progress as described in Section 1.5. It is therefore the intent of this study to focus on potential treatment technologies that are not "biological" in nature.

2.2 Approach

The study will assess the feasibility of each potential technology based on the following items:

- Technical effectiveness
- Implementability
- Cost-effectiveness
- Acceptance

2.3   Technology Review Methodology

In 1994, a literature search was conducted by an Aerojet consultant to identify technologies that were effective or had the potential to be effective in treating perchlorate in groundwater. This study also included a literature search to locate information on technologies that may have been developed since 1994 and to locate additional performance information on technologies identified in 1994. Because limited information specific to perchlorate treatment technologies was found, the scope of the search was broadened to include treatment technologies for other related chemical classifications, namely aqueous solutions, nitrate, brackish waters, and chlorine dioxide.

The database search consisted of online searching using Dialog and the Internet. Dialog is an online database service that allows access to documents in more than 650 discrete databases, approximately 150 of which are science related. Dialog is known for its collection of intellectual property data and was selected as the primary service to conduct this technology screen. The key to conducting thorough and meaningful research sessions using Dialog and the Internet is to focus on and identify as many key words as are applicable. The online searches were performed iteratively to capture additional words and concepts uncovered during the review of retrieved information. A list of databases searched and key words used during the online Dialog search are provided in Appendixes B and C, respectively.

3.0 PHYSICAL AND CHEMICAL PROPERTIES OF PERCHLORATE

This section provides a general overview of the available information relating to perchlorate in order to understand and recommend appropriate treatment options for perchlorate in groundwater. Subsection 3.1 provides a general description of perchlorate and its general chemical application or use. Subsection 3.2 discusses the chemical and physical properties of perchlorate. Subsection 3.3 identifies similarly structured compounds. Because treatment consideration of perchlorate is relatively new and treatment options specific to perchlorate are limited, the review of potential treatment technologies was expanded to include those applicable for similar ionic species such as nitrate. Finally, subsection 3.4 summarizes the current regulatory status of perchlorate.

3.1 General Description and Chemical Use

Forms of perchlorate include ammonium perchlorate, potassium perchlorate, sodium perchlorate, and perchloric acid. Ammonium, potassium, and sodium perchlorate are salts that readily dissolve and dissociate in groundwater. In an aqueous environment, the perchlorate anion (chemical formula ClO_4^-) remains dissolved in solution.

Perchlorate has been historically used as an oxidizer in rocket propellants, explosives, flares, and fireworks, and residual concentrations have been found in groundwater near several former explosive manufacturers and aerospace facilities. The reason that perchlorate (ClO_4^-) is useful in rocket fuel is that it is an excellent oxidizer (i.e., it gives up the 4th oxygen quite readily). Perchloric acid is used for metals etching and cleaning. In the presence of reducing agents, perchlorate can be reduced to chlorate (ClO_3^-) chlorite (ClO_2^-), hypochlorite (ClO^-), and ultimately, chloride (Cl^-), although the specific chemical kinetics involved in this reduction are unknown.

3.2 Physical and Chemical Properties

Specific physical and chemical properties of perchlorate salts are presented in Table 3-1.

3.3 Identification of Similar Compounds

As a result of recent advances in analytical methods allowing lower detection limits, the widespread identification of perchlorate in groundwater is relatively new. Consequently, the current number of treatment technologies relating strictly to removal of low concentrations of perchlorate is very limited. As

part of this technology screening, therefore, it was imperative that treatment technologies for other ionic compounds with similar properties be evaluated for potential applicability.

This approach is validated by recent pilot-scale testing for treatment of perchlorate at Aerojet's Sacramento facility. While nitrate concentrations present in the influent groundwater were observed to be approximately 1.5 mg/L, the effluent concentrations were shown to be less than 0.05 mg/L (HLA, 1997a). The significant reduction of nitrate illustrates two points: (1) the reduction of nitrate occurs under conditions required for the reduction of perchlorate and therefore denitrification technologies may be applicable, and (2) if nitrate, an anion, undergoes reduction similar to perchlorate, there is the possibility that other anions may react in a similar manner, some of which may also already have proven and effective means of treatment.

Nitrates in groundwater is a widespread problem in many areas including the San Gabriel Basin. The presence of nitrate in groundwater is due to the leaching of agricultural lands, leakage from septic tanks, leaching of lands used for raising animals, and application of nitrogen-rich fertilizers to turfgrass. Fortunately, significant progress has been made in the development of denitrification technologies. Therefore, denitrification technologies were considered for potential applicability during this investigation.

Various desalination technologies were also considered for potential applicability to perchlorate treatment. Because of the broad definition of salts, desalination technologies were reviewed with special consideration of technologies proven to remediate monovalent salts (i.e., anions with a singular electron charge, similar to the perchlorate ion). Expanding the search of alternative treatment technologies to desalination and denitrification provided a wider range of potential treatment technologies.

3.4   Regulatory Levels for Perchlorate

Perchlorate is not a regulated compound under the federal Safe Drinking Water Act. Therefore, limited data are available regarding its occurrence. At this time, perchlorate is regulated only in California. California's provisional action level of 18 μg/L was set in February 1997 by the California DHS. Because of the lack of toxicological data regarding the long-term effects of low concentrations of perchlorate on human health, a conservative approach was taken in setting the provisional action level. Additional detail on this subject can be found in HLA, 1997a.

4.0 IDENTIFICATION OF CANDIDATE TECHNOLOGIES

A technology review was performed to identify groundwater and wastewater treatment technologies that have demonstrated effectiveness or potential application to the treatment of perchlorate. The technologies identified fell into the three broad areas, physical, chemical, and biological. These broad areas contained specific technologies which are described below.

Physical treatment processes are those used for the treatment of water or wastewater in which a physical process is used to change or alter the properties of the target contaminant. The applicable physical treatment technologies include:

- <u>Sorption</u>

  - Adsorption using granular activated carbon
  - Ion exchange
  - Capacitative deionization
  - Gettering with reversibly dispersible carriers

- <u>Membrane Separation</u>

  - Reverse osmosis/nanofiltration
  - Electrodialysis

Chemical treatment processes are those used for the treatment of wastewater in which a chemical reaction is used to change or alter the properties of the target contaminant. The applicable chemical treatment technologies include:

- <u>Chemical Reduction/Oxidation</u>

  - Supercritical water oxidation
  - Chemical oxidation
  - Chemical reduction
  - Electrochemical reduction
  - Catalyzed chemical reduction

- Photocatalytic reduction

• Precipitation

Biological treatment is not included in this technology screening; however, its applicability to the treatment of perchlorate is discussed in Section 1.0, plans for pilot-scale testing can be found in HLA 1997c, and a comparative cost estimate is developed in Section 6.0.

4.1 Sorption Technologies

Adsorption and ion exchange share so many common features that they are grouped together here as sorption technologies. Both processes involve removal of a soluble contaminant (solute) from the solvent by contact with a solid surface (the adsorbent). These processes involve the transfer and resulting equilibrium distribution of one or more solutes between a fluid phase and particles. The partitioning of a single solute between fluid and sorbed phases or the selectivity of a sorbent toward multiple solutes makes it possible to separate solutes from a bulk fluid phase or from one another.

The design of sorption systems is based on a few underlying principles. First, the selection of the sorbent material with an understanding of its equilibrium properties (i.e., capacity and selectivity as a function of temperature and component concentrations) is of primary importance. Second, it is crucial to understand fixed-bed performance in relation to adsorption equilibrium and rate behavior. Finally, for processes where the regeneration of the sorbent is necessary, knowledge of aging characteristics of the sorbent and the associated changes in sorption equilibrium are needed. Typically, the effluent concentration of a sorption-based technology is closely monitored for "breakthrough." The effluent concentration stays at or near zero or a low residual concentration until the transition reaches the column outlet. The effluent concentration then rises until it becomes unacceptable, this time being called the breakthrough time. The feed step must stop and, for a regenerative system, the regeneration step begins.

The following sorption technologies have been identified as potentially applicable technologies for perchlorate treatment.

4.1.1 Activated Carbon

The adsorbent most widely used in environmental applications is carbon. Carbon that has been processed to significantly increase the internal surface area is referred to as activated carbon. Activated carbon is well suited for removal of mixed organic and aqueous contaminants. Activated carbon is a common adsorbent and is available in both powdered and granular form. Granular activated carbon (GAC) is most

commonly used for removal of a wide range of organic compounds or ions from groundwater and industrial waste streams. A typical GAC contactor is shown on Figure 4-1.

The effectiveness of carbon adsorption is dependent in part on a contaminant's aqueous solubility. The more hydrophobic (insoluble) a molecule is, the more readily the compound is adsorbed. The degree to which a compound or ion is adsorbed onto carbon is also dependent on the ion or compounds polarity. Highly polar ions or compounds are not well adsorbed (e.g. perchlorate), while less polar compounds adsorb well (e.g. benzene).

Activated carbon removes the ion or compound of concern from the fluid. Because this is not a destructive technology the contaminant of concern remains bound to the carbon Therefore the carbon must be changed out and replaced with fresh carbon. As carbon is quite expensive it is economically necessary to regenerate it. Therefore a significant maintenance consideration for systems using activated carbon treatment is the regeneration of spent carbon. Carbon can be regenerated by either thermal regeneration or nondestructive regeneration processes. Thermal oxidation involving the use of a multiple-hearth, fluidized-bed, or rotary kiln furnace is the most common method of regenerating GAC.

Data available from a Valley County Water District GAC contactor (Big Dalton Well) provides a preliminary evaluation of the effectiveness of GAC for removal of perchlorate. The study indicates GAC can effectively reduce perchlorate concentrations below 18 μg/L for a limited period of time. The data from the study are presented on Figure 4-2 and discussed in Section 5.0.

4.1.2   Ion Exchange

Ion exchange is a well established technology for the removal of cations (ions of positive charge) and anions (ions of negative charge) from dilute solutions. In ion exchange cations or anions present in the fluid (usually an aqueous solution) exchange with ions of the same charge initially adsorbed to the solid. The ion exchanger contains permanently bound functional groups of opposite charge type.

Ion exchange may be thought of as a reversible reaction involving chemically equivalent quantities. A common example for cation exchange is the familiar water-softening reaction:

$$Ca^{++} + 2NaR = CaR_2 + 2Na^+$$
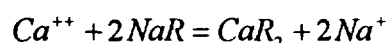
where R represents a stationary univalent negatively charged site on the exhanger surface.

A typical fixed-bed ion exchanger (Figure 4-3) consists of a vertical cylindrical vessel of lined steel or stainless steel. Linings are usually of natural or synthetic rubber. Spargers are provided at the top and

bottom, and frequently a separate distributor is used for the regenerant solution. The resin bed, consisting of a meter or more of ion-exchange particles, is supported by the screen of the bottom distributor. Externally, the unit is provided with a valve manifold to permit downflow loading upflow backwash, regeneration, and rinsing. For deionization, a two-exchanger assembly comprising a cation and an anion exchanger is a common configuration.

Except in very small-scale applications, ion exchangers are used in cyclic operations involving sorption and desorption steps. A typical ion-exchange cycle used in water-treatment applications involves (1) *backwash*—used to remove accumulated solids obtained by an upflow of water to expand (50-80 percent expansion is typical) and fluidize the exchanger bed; (2) *regeneration*—a regenerant is passed slowly through and used to restore the original ionic form of the exchanger; (3) *rinse*—water is passed through the bed to remove regenerant from the void volume and, in the case of porous exchangers, from the resin pores; (4) *loading*—the fresh solution to be treated is passed through the bed until leakage begins to occur.

Like adsorption, ion exchange is not a destructive technology. The ion exchange process merely removes an ion, like perchlorate, from water but concentrates it on the resin. Through regeneration the perchlorate is flushed from the resin but is then present in a small volume regenerating solution at very high concentrations. Therefore, use of ion exchange necessitates consideration or treatment and disposal of waste regenerating solution, in this case containing high concentrations of perchlorate.

At Aerojet's facility in Sacramento, laboratory and pilot-scale testing was specifically performed to reduce perchlorate concentrations in groundwater from 7 to 8 mg/L down to nondetect (<400 μg/L) by ion exchange methods. The results indicated that ion exchange was effective in reducing the perchlorate concentration to below the 400 μg/L laboratory detection limit. The process involved passing the affected groundwater through an ion-exchange resin where ions of perchlorate, sulfate, and nitrate substitute for the resin's chloride ions, leaving a perchlorate-free effluent. Upon regenerating the column, a perchlorate high (3000 mg/L) regenerant stream was produced that required further treatment. This regenerant stream was reduced in volume using electrodialysis, and then the perchlorate biochemically reduced to chloride.

4.1.3 Capacitive Deionization

Capacitive deionization (CDI) with carbon aerogel is a new technology used for the deionization of water and the treatment of aqueous wastes. It eliminates some of the waste generation and waste treatment/disposal problems inherent in ion exchange by substituting non-toxic and nonpolluting electricity for the acids, bases, and salts. CDI with carbon aerogel is electrically regenerated. This

technology is not however a destructive technology and the waste stream produced when regeneration is performed will contain high concentrations of perchlorate.

This patented technology (U.S. Patent No. 5,425,858 [see Appendix D]) issued on June 20, 1995, is a process for removing salt and impurities from water. The designated assignee are the regents of the University of California, Oakland, California. The patent describes the method and apparatus for capacitive deionization, electrochemical purification, and regeneration of electrodes. Further development of this technology has included effective removal of perchlorate from waste streams.

The process involves passing a stream of electrolytes, which contains various anions and cations, electric dipoles, and/or suspended particles through a stack of electrochemical CDI cells (Figure 4-4). Each of these cells includes numerous carbon aerogel electrodes having exceptionally high specific surface areas. Each electrode includes a single sheet of conductive material having a high specific surface area and sorption capacity. The sheet of conductive material is formed of carbon aerogel composite.

In operation, water to be treated enters the cell, and flows through a continuous open serpentine channel defined by the electrodes, substantially parallel to the surfaces of the electrodes. Every other electrode is an anode, starting with the end electrode, and ending with the intermediate electrode, and the remaining intermediate electrodes and the end electrode are cathodes. As such, each pair of adjacent electrodes (anode and cathode) forms a separate CDI/regeneration unit.

By polarizing the cells, ions are removed from the fluid stream electrostatically and held in the electric double layer formed at the carbon aerogel surface. Some metal cations are removed by electrodeposition. Small suspended particles are removed by electrophoresis. The cell is periodically regenerated by reversing the cell polarity. This significantly minimizes the volume of waste solution but presents the same challenge as adsorption and ion exchange as high concentration perchlorate solutions must be treated.

4.1.4 Getters and Reversibility Dispersible Carriers

One patent was identified that employed an adsorption process using getters and reversibly dispersible carriers. According to the patent (U.S. Patent No. 5,078,900 [see Appendix D]), which was issued January 7, 1992, the process is highly efficient and effective for removing a wide variety of dissolved contaminants such as metal ions, nonmetal ions, and dissolved organic contaminants such as dyes. HLA has contacted the designated "assignee" of the patent, Tiegel Manufacturing Company (Tiegel), to obtain more information regarding process applicability. Tiegel currently employs the process for removal of lead. To

date, HLA has not been able to obtain the information necessary to fully evaluate this technology. With this caveat (e.g., unknown applicability) to perchlorate or anions, the following information concerning the patent is provided.

According to the patent, a getter and a reversibly dispersible carrier are mixed with a contaminated aqueous solution in a dispersed state. The getter and dissolved contaminant form a getter-contaminant material that is believed to be in the form of a complex. The getter-contaminant material is then removed by reducing the dispersibility of the carrier in the aqueous solution to form a separate phase. This phase can be either liquid or solid. A suitable carrier must be sufficiently water insoluble so that excessive amounts of the carrier compound do not dissolve in the aqueous solution. However, the carrier must also be dispersible on an essentially molecular level in water so that it may be placed in a dispersed state.

In this process, a getter compound must be placed in a dispersed state. This may be achieved by dispersing the getter with a carrier compound directly in the contaminated aqueous solution or by predispersing the getter and carrier in a stock aqueous dispersion that is subsequently contacted with the contaminated aqueous solution. A stock dispersion may be prepared using known dispersing techniques such as using dispersing agents, heating, or adjusting the pH of the water. The particular method of placing the getter and carrier in a dispersed state will largely depend upon the pH, temperature, and ion composition of the contaminated aqueous solution.

After the contaminated aqueous solution has been contacted with a getter and carrier in dispersed state to form a getter-contaminant material, typically a getter-contaminant complex, the getter-contaminant material may be removed. The getter-contaminant material in the discontinuous phase may be separated from the aqueous solution using known techniques such as filtering, flocking, and/or settling. The getter and carrier may be regenerated using techniques generally known for regenerating contaminant loaded extractants in solvent extraction processing.

The result of treatment using this technology, if an appropriate getter and carrier can be found, is a carrier phase that although lower in volume than the fluid being treated will still contain high concentrations of perchlorate. This carrier will then need to be subjected to another treatment technology to reduce the perchlorate to chloride or some other means of carrier disposal will be needed.

4.2   Membrane Separation Technologies

Membrane separation technologies are employed widely throughout the world. Thousands of tons of drinking water are produced every day by passing pressurized seawater across a very thin membrane.

Ultrapure water used in the manufacturing of microchips is produced by passing water through membranes. Municipalities depend on electrodialysis to remove salt from brackish aquifers to provide high-quality potable water. Figure 4-5 illustrates the relative differences in membrane separation technologies. For purposes of this document, the membrane technologies discussed in detail are reverse osmosis and electrodialysis.

4.2.1   Reverse Osmosis

Reverse osmosis (RO) separates a solute from a solution by forcing the solution to flow through a membrane by applying a pressure greater than the normal osmotic pressure. The term reverse osmosis is generally used to describe the processes in which the solute molecules are about the same size the solvent molecules, whereas ultrafiltration is used for the separations involving solutes whose molecular dimensions are ten or more times larger than those of the solvent and are below 1/2 micron size. Such a separation process based on pressure difference across a membrane combines technical simplicity with versatility. Unlike distillation and freezing processes, it can operate at ambient temperature without phase change. RO is used to reduce the concentrations of both organic and inorganic dissolved solids. RO is an effective treatment technology for removal of dissolved solids presuming appropriate pretreatment has been performed for suspended solids removal, pH adjustments, and removal of oxidizers, oil, and grease.

The largest applications for RO, and most membrane processes, are brackish water desalination for drinking water and seawater desalination. In desalination, when water transfers through a membrane, the salt left behind concentrates in a solution next to the membrane surface. The efficiency of membrane separation therefore decreases as the concentrated salt solution layer gradually increases its thickness. Accompanying the increase in salt concentration at the interface is an increase in the osmotic pressure of the solution at the interface, which in turn decreases the pressure for driving water through the membrane. The salt layer built up near the membrane surface may reach a constant thickness as a result of a balance of two opposing factors, i.e., the convective transport of salt toward the membrane by the bulk motion of the water and the back diffusion of salt away from the membrane surface due to the gradient established near the phase boundary.

In desalination, the most effective membrane film is cellulose acetate. The membrane is made in a form of composite film in which a thin dense layer estimated to be 0.1 to 10 microns thick is supported by a much thicker (2 to 5 mils) porous, spongy substrate with little or no resistance to permeation. This type of membrane is referred to as an asymmetric membrane. Rejection efficiencies of various solutes by a modified cellulose acetate membrane are shown in Table 4-1. The compounds most effectively excluded

by the membrane are salts of divalent ions, sucrose, and the tetralkyl ammonium salts. The apparent permeabilities of water and the various solutes were calculated based on the effective membrane thickness of 0.16 micron. It is also noted that a high separation percentage of various salts, particularly magnesium perchlorate ($Mg[ClO_4]_2$) was obtained (90-95%). Additional information about this experiment is presented in a paper by M. Malaiyandi and V.S. Sastri (included in Appendix E).

A membrane suitable for RO processes has to meet stringent requirements. For example, some important membrane properties in relation to the process economics of desalination are (1) membrane selectivity for water over ions, which determines the number of pressurized stages required to produce potable water; (2) permeation rate of water per unit pressure gradient, which determines the size of the equipment per unit production rate of potable water; and (3) membrane durability, which determines how often the membrane must be replaced.

There are four common membrane module designs. These are plate-and-frame, spiral-wound, tubular, and hollow-fiber. The plate-and-frame type has several variations used in the industry today. The most common one consists of thin plastic plates covered on both sides by membranes that are sealed around the edge to prevent leaks. These plates resemble phonograph records in that their flat surfaces contain small grooves through which the permeate flows after passing through the membrane. The permeate eventually flows into a central tube at the stack and is collected through this tube.

In reverse osmosis the dissolved salts or ions are excluded from the effluent stream and concentrated in a waste brine. The volume of this waste will vary with the membrane type, operating conditions, and the influent composition and commonly varies from 10 to 30 % by volume of the influent water. In the case of treatment for perchlorate this waste brine will contain all the perchlorate mass removed from the treated groundwater. Treatment of this waste brine will be needed prior to disposal.

4.2.2   Electrodialysis

Electrodialysis (ED) is a membrane process in which ionic components of a solution are separated through the use of semipermeable ion-selective membranes. In electrodialysis, the concentration and/or composition of electrolyte solutions is altered as a result of electromigration through membranes in contact with these solutions. Ion migration under action of electric current causes salt depletion in alternate compartments and salt enrichment in adjacent ones. In industrial electrodialysis installations, which contain from ten to hundreds of compartments between one pair of electrodes, the passage of electric current thus creates fresh water ("diluate") and brine in neighboring cells. In other words, half the

cells carry partly desalted water and half carry brine. This results in the separation of the ionic species from water. Figure 4-6 illustrates the principles of electrodialysis.

ED has its greatest use in removing salts from brackish water, where feed salinity is around 0.05-0.5 percent. For producing high-purity water, ED can reduce solute levels to extremely low levels as a hybrid process in combination with an ion-exchange bed. Many electrodialysis-related processes are practiced on a small scale, or in unique applications. ED is effective at separating electrolytes from nonelectrolytes and concentrating electrolytes to high levels, however, ED is not effective in removing the last traces of salt at high pH, tolerating surfactants, or running under conditions where solubility limits may be exceeded.

The solutions in the electrode compartments are contaminated with the products of the electrode reactions which take place as a result of the passage of the current (Perry and Chilton, 1973). The electrodes must be continually rinsed to prevent buildup of hydrogen gas at the cathode and oxygen or chlorine at the anode. Typical electrodialysis units operate at pressures in the order of 276 to 414 kPa (40 to 60 psi). Generally, 90 percent of the feed is transformed to product water, while approximately 10 percent remains as the concentrate. (LaGrega, et.al., 1994).

Modern electrodialysis cell designs have incorporated the periodic reversal of current to reduce fouling of the membrane. Buildup of precipitated salts is dissolved and carried away when the cycle reverses. Additionally, automatic valves change the feed/product stream to the brine compartments and switch the brine stream discharge to the feed/product compartments. Both streams are automatically diverted as waste for approximately 1 to 2 minutes due to their high salinity. This process disperses polarization films, reduces slime and colloidal fouling, and flushes scaling deposits out of the electrodialysis system. To be effective, the polarity reversal has to be frequent enough to avoid the accumulation of heavy scale, and it must be supplemented with regular chemical cleaning (MacNeil, 1988).

In electrodialysis the dissolved salts or ions are excluded from the effluent stream and concentrated in high salinity waste brines. The volume of this waste will vary with the membrane type, potential applied across the cells, and the composition of the influent. Because this is a separation technology and is not destructive these high salinity wastes will contain the total perchlorate mass removed from the treated groundwater. Treatment of this high salinity waste will be needed prior to brine disposal.

Aerojet has performed bench-scale testing of electrodialysis process at the Sacramento facility for the treatment of wastewaters containing perchlorate. This technology was used to pre-concentrate perchlorate in the regenerant solution from ion exchange pilot-scale testing prior to biochemical reduction. Three

streams were formed: (1) a sodium hydroxide solution at the cathode, (2) a slightly basic solution containing essentially all of the perchlorate (and other anions), and (3) an acidic, water-depleted solution at the anode. All three wastes were successfully treated by biochemical reduction.

4.3 Chemical Oxidation and Reduction Reactions

Chemical reduction/oxidation alters the form of a chemical by loss or acceptance of electrons. For inorganic solutes, oxidation involves the loss and acceptance of electrons, but is more accurately defined as a reaction that increases the oxidation state of an atom (i.e., the charge on the atom becomes more positive). Conversely, reduction is defined as a reaction that decreases the oxidation state for an atom (i.e., charge on the atom becomes more negative).

Chemical reduction-oxidation (redox) reactions classically involve the gain or loss of oxygen. A reaction that adds oxygen to a compound is oxidation. Likewise, loss of oxygen (frequently with the addition of hydrogen) is termed reduction. However, oxidation-reduction reactions do not necessarily involve oxygen.

Parameters that can be used to quantify treatment effectiveness are the free energy of a reaction and the oxidation reduction potential. Factors such as temperature and pH, the presence of catalysts, and concentration of other reactants will influence selection of the oxidizing agent or reducing agent and will determine whether a treatment is feasible and economical.

An indication of how a reaction will proceed can be determined from the free energy considerations (see Sec. 3-3). The free energy of a reaction, $\Delta G°$, is related to the standard electrode potential $E°$, and the equilibrium constant K by:

$$\Delta G° = -nFE° = -RT \ln K$$

where

$\Delta G°$	=	free energy of a reaction (kcal/gmol)
n	=	number of electrons exchanged during the reaction per gmol
F	=	Faraday constant 23.062 kcal/(volt-equiv.)
$E°$	=	standard electrode potential (volts)
R	=	gas constant = 1.98×10^{-3} kcal/gmol · K
T	=	temperature (K)
K	=	reaction equilibrium constant

$E°$ may be determined from tabulated half-reactions. To assemble a complete reaction from two half-reactions, an oxidation half-reaction is added to a reduction half-reaction (LaGrega et al., 1994).

A major consideration in electing to utilize oxidation or reduction technology is that the treatment chemicals are potentially hazardous, and great care must be taken in their handling. In some cases, undesirable byproducts may be formed as a result of oxidation. For example, addition of chlorine can result in formation of bioresistant end products that can be odorous and more toxic than the original compound.

The following chemical reduction and oxidation technologies have been identified as applicable technologies for perchlorate treatment.

4.3.1 Chemical Oxidation

Although the perchlorate ion is fully oxidized, oral information has been received from agencies in Nevada and California regarding the effectiveness of ozone and hydrogen peroxide in reducing perchlorate concentrations. The decomposition mechanism is not understood.

Chemical oxidation is typically conducted in completely mixed tanks or plug flow reactors. The contaminated water is introduced at one side of the tank and the treated water exits at the other side. The oxidizing agent is either injected into the contaminated water just before it enters the tank or is dosed directly into the tank. Complete mixing of the water with the oxidizing agent must be provided, either by mechanical agitation, pressure drop, or bubbling into the tank. Complete mixing, which prevents short-circuiting in the tank, is necessary to ensure contact of the contaminants with the oxidizing agent for a minimum period of time and thus reduce the chemical dosage required to obtain a specific effluent concentration (ERM-West, 1996). Ozone and hydrogen peroxide are two common oxidizers.

Ozone is produced from atmospheric oxygen using electrical energy to split the oxygen into two oxygen radicals (O $\cdot$), which readily combine with other oxygen molecules (O_2) to form ozone (O_3). Ozone is unstable under normal environmental conditions and readily decomposes back to oxygen.

Hydrogen peroxide is another powerful chemical oxident. Hydrogen peroxide (H_2O_2) and UV light are generally used together. Hydrogen peroxide is used as a 35 to 50 percent solution. The high solubility of H_2O_2 in water obviates the need for mixing equipment, reducing the number of moving parts in the system. The size of the combined H_2O_2/UV system can be significantly reduced through the use of high-energy UV lamps, capable of imparting 500 Watts/Liter to the water.

4.3.2   Supercritical Water Oxidation

A chemical oxidation process known to treat perchlorate ion is supercritical water oxidation. According to a 1993 paper (Harradine et al., 1993) supercritical water oxidation is a chemical treatment process that involves mixing waste with an oxidant (such as oxygen, air, or hydrogen peroxide) in supercritical water (conditions above 218 atmospheric pressure and 374°C). The resulting gaseous properties of the supercritical water allows chemical reactions to proceed more rapidly, and oxidation can take place at temperatures significantly lower than for incineration. The process is applicable to a broad range of waste types (both solid and liquid) and typically results in complete destruction of the materials to be treated. Bench-scale linear flow reactors have been developed to destroy explosives in supercritical water. A schematic of a linear flow reactor is shown in Figure 4-7. Additional information regarding this process as presented in the paper (Harradine et al., 1993) is included in Appendix E.

This process allows a high throughput of waste to be processed. Because high temperatures and pressures must be maintained, cost associated with this process are relatively high, especially for low concentrations of waste constituents.

4.3.3   Chemical Reduction

In 1995 Aerojet tested the effectiveness of several common chemical reducing agents, sodium bisulfite, sodium sulfite, and sodium thiosulfate on perchlorate in water. These chemicals were mixed with the water containing 7,000 to 8,000 μg/L in a reaction vessel to induce a chemical reaction whereby the perchlorate becomes reduced to chloride. This method was demonstrated not to be effective at dosages of reducing agent as high as 1,000 mg/L; however, there may be other chemical reducing agents that are effective.

4.3.4   Electrochemical Reduction

The electrochemical process is a physical/chemical process that uses an anode and cathode separated by a cation exchange membrane. A patent (U.S. Patent No. 5,167,777) was issued in 1992 for electrochemical treatment of aqueous solutions containing inorganic oxyhalide species. The focus of the patent is on the treatment of chlorine dioxide, although the process is also applicable for treatment of perchlorate. The process involves applying an electrical current between the anode and cathode while the water to be treated is fed through the process cell containing the cathode (Figure 4-8). The oxyhalide species in the water are electrochemically reduced on the cathode surface to produce chloride ions, and the treated water then exits the cathode cell. A patent was issued in 1992 for electrochemical treatment of aqueous solutions containing inorganic oxyhalide species.

4.3.5   Catalyzed Chemical Reduction

A catalyst is a substance that increases the rate of a reaction by participating chemically in intermediate stages of reaction and is ultimately liberated in a chemically unchanged form. Inhibitors are substances that slow down rates of reaction. The turnover ratio, the number of molecules converted per molecule of catalyst, can be in the millions. Many catalysts have specific actions in that they influence only one reaction or group of definite reactions. When a reaction can proceed by more than one path, a particular catalyst may favor one path over another and thus lead to a product distribution different from an uncatalyzed reaction. A catalytic reaction requires a lower energy of activation, thus permitting a reduction of temperature at which the reaction can proceed favorably. The equilibrium condition is not changed since both forward and reverse rates are accelerated equally.

4.3.6   Photocatalytic Reduction

Photocatalysis is an emerging water treatment technology. When a semiconductor photocatalyst, for example, titanium dioxide (TiO_2), is illuminated with ultraviolet (UV) radiation, the impinging UV photons excite valence band electrons across the bandgap into the conduction band, leaving holes behind the valence band. If the semiconductor is immersed in water, the holes react with water molecules (H_2O) or hydroxide ions (OH^-) and produce hydroxyl radicals ($OH^•$), very strong oxidants capable of oxidizing many organic compounds. Hydroxyl radical oxidation is thought to be the primary mechanism for destruction of organic compounds; however, other direct and indirect reactions may occur. These side reactions may lead to reduction of 1/2 organic compounds.

The UV radiation used in photocatalysis may come from the sun or an artificial source. However, to generate electron-hole pairs, the incident photons must have an energy greater than the bandgap of a semiconductor photocatalyst. For the widely used anatase form TiO_2, the bandgap is 3.2 eV, which corresponds to a UV wavelength of 387.5 mm. Therefore, the 300 to 387.5 mm portion of solar insolation available on the ground level may be used with this photocatalyst. A wide spectrum of organic contaminants in water (for example, benzene and phenol, ketones, ethers, pesticides, chlorinated aliphatic, and aromatic compounds such as trichloroethylene and polychlorinated biphenyls, and other halogenated compounds) has been photocatalytically treated into nontoxic forms, such as simple mineral acids, carbon dioxide, and water. Additional information regarding this process as presented in the paper (Zhang, et al., 1994) is included in Appendix E.

4.4   Chemical Precipitation

Precipitation is a chemical process in which some or all of a substance in solution is transformed into a solid phase. It is based on the alteration of the chemical equilibrium relationships affecting the solubility of inorganic species. Chemical precipitation in wastewater treatment involves the addition of chemicals to alter the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation. In some cases the alteration is slight, and removal is effected by entrapment within a voluminous precipitate consisting primarily of the coagulant itself. Another result of chemical addition is a net increase in the dissolved constituents in the wastewater. Chemical processes, in conjunction with various physical operations, have been developed for the complete secondary treatment of untreated wastewater, including the removal of either nitrogen or phosphorus or both.

A paper published in 1996 describes the testing of perchlorate-specific precipitation reagent for aqueous solution. The article entitled "The Synthesis, Characterization, and Testing of a Reagent for the Selective Removal of Dichromate and Perchlorate from Aqueous Solution" (Kopchinski, and Meloan, 1996), described a reagent that will selectively precipitate perchlorate from water. According to the study, this reagent, N-4-Vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane, was tested with 51 common anions to determine the selectivity of the reagent. Based on these tests, it was determined that only six anions (perchlorate included) formed an immediate precipitate. Three additional anions formed a precipitate after 2 hours while the remaining anions tested did not precipitate out, making the reagent highly selective. The positive application of this reagent is that in addition to the precipitation of perchlorate, many of the anions that may be present in the extracted groundwater (i.e. nitrate, nitrite, fluoride, hydroxide, cyanide, carbonate, chlorate, chloride, etc.) will not be selectively precipitated, thereby significantly limiting the quantity of sludge produced. It should be noted that the concentrations tested in this experiment were much higher than the perchlorate concentrations present in the influent (10,000 mg/L which is approximately 100,000 times the concentration of perchlorate in the extracted groundwater). Therefore, it is unknown whether this reagent will be effective in precipitating perchlorate down to the 18 μg/L action level.

No other chemical precipitation technologies were identified for perchlorate ion; however, a patented technology was identified that involved the implementation of precipitation as a treatment technology for the removal of nitrates. Because of the similarities between perchlorate and nitrate ion, this technology is considered potentially applicable.

U.S. Patent No. 5,266,201 (assigned to Lafarge Fondu International, 1993), describes a process for the purification of aqueous solutions polluted by nitrate ions. This process is characterized by precipitating hydrated double or mixed calcium nitroaluminates, by adding at least one agent supplying the element aluminum and at least one agent supplying the element calcium to the solutions to be treated. The precipitation reaction is performed with stirring and at a basic pH, preferably above 10.5, and where appropriate, the precipitate obtained is removed, for example, by flocculation followed by one or more settling and physical separation and/or filtration operations.

Precipitation and flocculation are well-established technologies and the operating parameters are well defined. The processes require only chemical pumps, metering devices, and mixing and settling tanks. The equipment is readily available and easy to operate. Precipitation and flocculation can be easily integrated into more complex treatment systems. The performance and reliability of precipitation and flocculation depend greatly on the variability of the composition of the waste being treated. Chemical addition must be determined using laboratory tests and must be adjusted with compositional changes of the waste being treated or poor performance will result.

This process is not destructive and would result in a flocculated solid containing high concentrations of perchlorate. A primary safety concern relates to the precipitation of a solid containing perchlorate at potentially explosive levels. Disposal or treatment of this solid would present a technical challenge.

5.0 INITIAL TECHNOLOGY SCREENING

This section describes the rationale that was developed to evaluate and screen technologies presented in Section 4.0. The purpose of this screening was to evaluate on a comparative basis a wide range of applicable and potentially applicable perchlorate treatment technologies and identify which of these technologies show the greatest promise for achieving the project objectives. The results of this are presented following a summary of screening criteria. The technologies that show the greatest promise, based on current information and assumptions, are subjected to a more thorough evaluation in Section 6.0.

5.1 General Assumptions

To screen technologies described in Section 4.0, several general assumptions were made. First, it has been assumed that the BPOU project will extract groundwater from two general areas at a combined rate of approximately 20,000 gpm. Second, it has been assumed that this extracted groundwater will be conveyed to a central treatment plant with sufficient land to add a perchlorate treatment unit. Third, it has been assumed that influent water quality will be similar to that previously estimated, containing between 50 and 100 μg/L perchlorate and 15 to 25 mg/L nitrate. Fourth, it has been assumed that perchlorate treatment will be a unit process that follows VOC removal. Fifth, it has been assumed that treated water must be potable.

It should be noted that the fourth assumption may be revised as further work on perchlorate treatment proceeds. The BPOUSC will, following this screening of perchlorate treatment technologies, assess whether any of these technologies would contribute to or could replace VOC treatment by air stripping. Additionally, the possible removal of perchlorate prior to VOC removal will be evaluated.

5.2 Screening Criteria

The criteria by which technologies identified in Section 4.0 as being applicable or potentially applicable for the removal of the perchlorate ion from groundwater were screened are presented in Table 5-1. To compare technologies objectively with respect to perchlorate treatment, each technology was evaluated with respect to four factors: effectiveness, implementability, cost, and acceptance. Three primary evaluation factors (effectiveness, implementability, and cost) are each divided into three subfactors. Each subfactor is ranked between 1 and 5 for each technology. The fourth factor, acceptance was also given a score between 1 and 5. The total score for each technology is tallied. A maximum score of 50 is possible.

5.3   Results of Initial Screening

The technologies screened are listed in Table 5-2. Technologies that rank highest are carried forward to Section 6.0 and subjected to a more detailed evaluation including the development of a conceptual design and cost estimate.

5.3.1   Alternative A-1: Biological—Biochemical Reduction

Bench- and pilot-scale studies performed by Aerojet have demonstrated the effectiveness of biochemical reduction in reducing concentrations of the perchlorate ion in groundwater. Pilot-scale studies to specifically address treatment requirements for San Gabriel Basin are currently being conducted. For comparison purposes, biochemical reduction is scored here.

Effectiveness. The technology can likely achieve the prescribed effluent standard (5), disinfection prior to delivery protects human health and the environment (3), and the technology is considered reliable (5). A total score of 13 is given for effectiveness.

Implementability. Biological treatment is a well-established technology with readily available components (5), requires small amounts of space (5), and has minimal process-related health and safety considerations (5). A score of 15 is given for implementability.

Cost. Biological treatment would require limited developmental costs assuming that data from Phase 1 and the Aerojet Sacramento system are available (5), capital costs will be comparatively small (5), and O&M costs are comparatively small (5). A score of 15 is given for cost.

Acceptance. Biological treatment is not widely used in public drinking water supplies and therefore may be of some concern. A score of 3 is given for acceptance.

The total score for biochemical reduction is 46 out of 50.

5.3.2   Alternative A-2: Adsorption—Activated Carbon

EPA provided data collected by the Valley County Water District for the Big Dalton liquid phase GAC treatment plant demonstrating that carbon removes the perchlorate ion from groundwater. The data are shown in Figure 4-2. No other adsorption isotherm for perchlorate ion on activated carbon was available.

Samples were gathered at the influent, effluent, and three intermediate points in the GAC contactor and analyzed for perchlorate concentration. Information regarding the sampling protocol, analytical method, system parameters, and carbon derivative (e.g., coal based) was not available, but for the purposes of this screening, it was assumed that the data are valid.

To evaluate this technology several conclusions were drawn. First, carbon adsorption can, at least initially, achieve the prescribed effluent standard. Initial data demonstrate no perchlorate ion was detected in the effluent immediately after fresh carbon was exposed to perchlorate ion. Second, the data for 19 and 24 days indicate that the perchlorate ion weakly adsorbs onto carbon and is in fact easily displaced or desorbed. This is expected since perchlorate ion is both ionic and very soluble. Third, the data suggest that some time between 7 and 12 days, the effluent from the GAC contactor exceeds the 18 $\mu g/L$ provisional action level, necessitating carbon changeout. Assuming that carbon is changed out every 7 days, the annual O&M cost for the BPOU project would be between $15 and $20 million per year.

The scoring for activated carbon adsorption is as follows:

Effectiveness. The technology can achieve the prescribed effectiveness standard in the effluent (5), is protective of human health and the environment (5), but may not be reliable due to rapid perchlorate breakthrough (1). A total score of 11 is given for effectiveness.

Implementability. Activated carbon adsorption is a well-established technology with readily available components (5), but will require significant engineering because of frequent carbon changeouts (1), and has moderate process-related health and safety considerations related to the onsite carbon regeneration facility (3). A score of 9 is given for implementability.

Cost. Carbon would require minimal developmental costs (5), capital costs could be significant because onsite regeneration would be required (1), and O&M costs would be extremely high because of carbon usage (1). A score of 7 is given for cost.

Acceptance. Carbon might meet some concern by due to reliability because of rapid breakthrough of perchlorate. A score of 3 is given for acceptance.

The total score for carbon adsorption is 30 out of 50.

5.3.3   Alternative A-3: Adsorption—Ion exchange

Aerojet conducted extensive bench-scale testing using ion exchange for the treatment of perchlorate ion in groundwater at its Sacramento facility. At least six different resins were tested for effectiveness. The viability of removing perchlorate from actual contaminated groundwater was demonstrated, accumulated perchlorate ion was removed from the exchange resin, resin was successfully recycled between exhaustion and regeneration phases, a final waste stream suitable for disposal was generated that was less than 1 percent by volume of the influent stream, and the system reliably operated with little attendance even after shutdowns of over a week.

The testing demonstrated that perchlorate ion can be removed to less than 400 μg/L, the laboratory reporting limit used at the time. The current laboratory reporting limit is much lower (4 μg/L). Ion exchange has not been demonstrated to meet the target effluent criterion, although detailed performance curves for perchlorate, sulfate, and nitrate suggest the goal can be met.

The largest concern with ion exchange centers around regeneration of the exchange resin and the associated waste stream management and operational costs. The regenerate stream was saline and contained high levels of perchlorate (3,000 mg/L). The stream was treated onsite by electrodialysis and then biochemical reduction. Biochemical reduction would require additional space, capital expenditures, and O&M costs.

The scoring for ion exchange is as follows:

Effectiveness. Ion exchange has been demonstrated to remove perchlorate ion to less than a laboratory reporting limit of 400 μg/L. The ability to achieve the prescribed effluent standard is likely (5), ion exchange generates a more concentrated waste stream that must be treated (3), and ion exchange is widely used in water treatment and is considered reliable (5). A total score of 13 is given for effectiveness.

Implementability. Ion exchange is a well-established technology with readily available components (5), and would likely require modest amounts of space to incorporate regeneration waste treatment (3). Ion exchange has minimal process-related health and safety considerations (5). A score of 13 is given for implementability.

Cost. Ion exchange would require minimal developmental costs (5), capital costs are moderate including onsite regeneration facilities (5), and O&M costs are anticipated to be moderate because of regeneration of the ion exchanger (3). A score of 13 is given for cost.

Acceptance. Ion exchange would likely be readily approved. A score of 5 is given for acceptance.

The total score for ion exchange is 44 out of 50.

5.3.4 Alternative A-4: Adsorption—Capacitive Deionization

CDI has a distinct theoretical efficiency over membrane and other adsorption technologies. First, CDI is inherently energy efficient. Secondly, CDI does not force the solute through any porous media and consequently the pressure drop is much lower than in conventional processes (water could conceivably flow through open channels). Third, CDI distributes carbon as an efficient and reliable mono-molecular layer. Fourth, the sorption medium is immobilized and will not become entrained in the water stream. Fifth, CDI efficiently distributes the electric potential across thin layers of carbon aerogel. Finally, CDI presents a higher specific surface area sorption media.

Extensive testing would need to be done to evaluate whether CDI is appropriate for large-scale application. A number of significant uncertainties are associated with this technology. Unknowns include the capacity and long-term characteristics of the carbon aerogel, full-scale equipment capital and operational costs, and whether other dissolved ions would degrade the efficiency of the system in the proposed application. Finally, additional treatment would be necessary for the regenerative waste stream. The composition and volume of this waste stream are unknown.

The scoring for CDI is as follows:

Effectiveness. The technology's effectiveness for perchlorate is likely good but unproven to reduce perchlorate to the effluent standard (3), effects on human health and the environment are expected to be minimal (5), and reliability is unknown (3). A total score of 11 is given for effectiveness.

Implementability. This technology is experimental (1), space requirements are unknown (3), and process health and safety considerations are unknown (3). A score of 7 is given for implementability.

Cost. This technology would require significant development costs (3), capital costs are uncertain (3), and O&M costs are uncertain (3). A score of 9 is given for cost.

Acceptance. This technology is unproven. A score of 3 is given for acceptance.

The total score for CDI is 30 out of 50.

5.3.5   Alternative A-5: Adsorption—Gettering with Reversibly Dispirsable Carriers

The getters and reversibly dispersible carrier (GRDC) process removes dissolved contaminants from aqueous solutions. The aqueous solution is contacted with a getter and a nonpolymeric, reversibly dispersible carrier in a dispersed state to form a getter-contaminant material; the getter-contaminant material is removed by reducing the dispersibility of the carrier to form a discontinuous phase containing the getter-contaminant material; the discontinuous phase is separated from the aqueous solution. The use of getters and reversibly dispersible carriers was described in a patent (No. 5,078,900) that was issued on January 7, 1992. This process is similar to liquid extraction, and GRDC has the potential to be applicable to perchlorate ion in water, but its effectiveness has not been demonstrated. This technology is experimental and there are several significant unknowns related to getter selection and dispersal.

If a suitable complexing getter could be identified, the process necessary to obtain dispersion may not be acceptable. Implementation of this technology could include altering the water temperature or pH, or the addition of salts or metal ionic species. These process steps will likely be both cost prohibitive and unacceptable to the regulatory agencies, public, and water purveyors.

The scoring for GRDC is as follows:

Effectiveness. The technology's effectiveness for perchlorate is unknown (1), a getter and carrier applicable to perchlorate are unknown and therefore effects on human health and the environment are uncertain (1), and reliability is unknown (1). A total score of 3 is given for effectiveness.

Implementability. This technology is experimental (1), large amounts of space would likely be required for carrier separation (1), process-related health and safety considerations are unknown (3). A score of 5 is given for implementability.

Cost. This technology would require significant development costs (1), capital costs are unknown (3), and O&M costs are unknown (3). A score of 7 is given for cost.

Acceptance. This technology is unproven. A score of 1 is given for acceptance.

The total score for GRDC adsorption is 16 out of 50.

5.3.6   Alternative A-6: Membrane technology—Reverse Osmosis

Reverse osmosis is a membrane technology where dissolved constituents are separated through membranes under applied pressure. Reverse osmosis has not been proven to remove perchlorate from water; however, since membranes are used to produce ultrapure water in a variety of applications, it is anticipated that RO could easily meet the targeted treatment standards. RO has the distinct advantage of being a highly proven and reliable method for removing ionic species from water.

Because of the nature of RO, operational issues drive technology costs. First, the membrane elements require significant maintenance to operate properly. The membrane elements can foul and must be chemically cleaned on a regular basis. Second, because of high operating pressures and maintenance issues, operating costs are high. Additionally, the reject effluent will contain high levels of perchlorate. The stream must be treated either on- or offsite. Biochemical reduction is a likely treatment process for this waste stream and would require additional space, capital expenditures, and O&M costs.

The scoring for RO is as follows:

<u>Effectiveness</u>. RO will likely achieve the prescribed effluent standard (5), RO generates a more concentrated waste stream that must be treated (3), and RO is widely used in water treatment and is considered reliable (5). A total score of 13 is given for effectiveness.

<u>Implementability</u>. RO is a well-established technology with readily available components (5), and would likely require modest amounts of space to incorporate regeneration waste treatment (3). RO has minimal process-related health and safety considerations (5). A score of 13 is given for implementability.

<u>Cost</u>. RO would require minimal developmental costs (5), capital costs could be significant because onsite treatment of reject water would likely be required (3), and O&M costs are anticipated to be high because of membrane maintenance and operational power requirements (1). A score of 9 is given for cost.

<u>Acceptance</u>. RO would likely be readily approved. A score of 5 is given for acceptance.

The total score for RO is 40 out of 50.

5.3.7 Alternative A-7: Membrane Technology—Electrodialysis

Electrodialysis is a proven water purification technology that is used where selected electrolytes are concentrated. Aerojet conducted bench-scale testing of ED for the treatment of perchlorate ion in groundwater at its Sacramento facility. The testing demonstrated that perchlorate ion can be removed to less than 400 μg/L, the laboratory detection limit used at the time. Current laboratory detection limits are much lower, 4 μg/L. ED can likely meet the target effluent criteria.

Several operational concerns were demonstrated in Aerojet's study. First, three process streams were formed: (1) a sodium hydroxide solution at the cathode, (2) a slightly basic solution containing essentially all of the perchlorate (and other anions), and (3) an acidic, water-depleted solution at the anode. Thus, pH adjustment will likely be necessary prior to discharge, and additional treatment will be required of the perchlorate-rich stream. Additionally, energy requirements are anticipated to be significant. Finally, hydrogen and oxygen gases form at the electrodes if they are not continually rinsed, which results in operational concerns.

The scoring for ED is as follows:

Effectiveness. ED has been demonstrated to remove perchlorate ion to less than a laboratory detection limit of 400 μg/L and can likely achieve the prescribed effectiveness standard (5), ED generates a more concentrated waste stream that must be treated and may require pH adjustment of product streams (1), and ED is widely used in water treatment and is considered reliable (5). A total score of 11 is given for effectiveness.

Implementability. ED is a well-established technology with readily available components (5), and would likely require only modest amounts of space to incorporate regeneration waste treatment (5). ED would have few process-related health and safety considerations (5). A score of 15 is given for implementability.

Cost. ED would require minimal developmental costs (5), capital costs could be significant for equipment and because onsite treatment of reject water would likely be required (3), O&M costs are anticipated to be high because of energy and treatment costs (1). A score of 9 is given for cost.

Acceptance. ED would likely be readily approved. A score of 5 is given for acceptance.

The total score for ED is 40 out of 50.

5.3.8   Alternative A-8: Oxidation—Chemical Oxidation

Chemical oxidation through the use of oxidizers such as ozone and hydrogen peroxide is a proven water treatment technology for destroying many organic compounds. Currently, the feasibility of chemical oxidation (utilizing ozone and hydrogen peroxide as oxidizing agents) for the treatment of perchlorate is being evaluated in San Gabriel Basin. Chemical oxidation has not currently, however, been demonstrated to be effective in reducing perchlorate concentrations to the target effluent level. Information received to date from vendors has been oral and unsubstantiated.

A concern regarding use of chemical oxidation is theoretical in nature and not substantiated for perchlorate. Based on oral communications with vendors, oxidation processes appear to reduce perchlorate concentrations; however, no supporting data have been provided. Since perchlorate ion is fully oxidized, the decomposition mechanism is unknown.

The scoring for chemical oxidation is as follows:

Effectiveness - Chemical oxidation has not been proven to reduce perchlorate to the desired standard (1), perchlorate decomposition byproducts are not understood (1); however, it is a proven, reliable technology (5). A total score of 7 is given for effectiveness.

Implementability - Chemical oxidation is a well-established technology with readily available components (5), would require moderate space (3), and has moderate health and safety concerns (3). A total score of 11 is given for implementability.

Cost - Chemical oxidation would require substantial developmental costs and the technology is unverified and mechanism unknown (1), would have relatively high capital costs due to equipment and construction necessities (1), and would have high operating costs due to oxidizer use and electrical consumption (1). A total score of 3 is given for cost.

Acceptance - Chemical oxidation would likely be accepted. A total score of 5 is given for acceptance.

The total score for chemical oxidation is 26 out of 50.

5.3.9   Alternative A-9: Oxidation—Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is an emerging technology for the destruction of organic compounds in water streams. It involves the elevation of water temperature and pressure to the "critical"

point (where the distinction between liquid and gas is no longer discernible). This process has been demonstrated to thermally decompose perchlorate.

Significant design considerations for SCWO exist, such as materials of construction to withstand extreme temperatures and pressures. Bench-scale experiments have demonstrated the need for a gold-lined reaction vessel to minimize liner corrosion. Furthermore, under some operating conditions, chlorine gas evolved.

The scoring for SCWO is as follows:

Effectiveness - SCWO has been demonstrated to treat perchlorate and can likely achieve the target concentration (5), effects on human health and the environment are uncertain (3), and may not be reliable due to the sensitive requirements (extreme temperature and pressure) of the process (1). A total score of 9 is given for effectiveness.

Implementability - SCWO is a relatively new technology (1), requirements for space are likely high and specialized (1), and it has significant process-related health and safety concerns (1). A total score of 3 is given for implementability.

Cost - SCWO would require significant developmental costs (1), capital costs would be relatively high based on the construction materials required (1), and operating costs would be relatively high (1). A total score of 3 was given for cost.

Acceptance - SCWO would meet with concerns regarding its effectiveness. A total score of 3 was given for acceptability.

The total score for SCWO is 18 out of 50.

5.3.10   Alternative A-10:   Reduction—Chemical Reduction

Chemical reduction involves the reduction of perchlorate ion to elemental oxygen and chlorine through the addition of chemical reducing agents. Selected chemical reduction agents have been tested at bench scale and shown not to be effective in reducing perchlorate concentrations. Aerojet conducted bench-scale testing of chemical reduction utilizing thiosulfate and bisulfite at room temperature and pressure. Chemical reduction is a potentially viable technology if an effective reducing agent can be found.

The disadvantages of a chemical reduction process involve adjustment of the influent stream pH, temperature, and pressure and the addition of chemical reduction compounds. First, a suitable reducing agent would need to be identified. Once this is accomplished, optimal reaction conditions need to be developed. Any reduction byproducts would have to be harmless in potable water. Finally, the effluent stream would have to be pH adjusted prior to discharge.

The scoring for chemical reduction is as follows:

Effectiveness. Previous studies showed the technology to be ineffective for perchlorate (1), suitable reducing agents applicable to perchlorate are unknown and therefore effects on human health and the environment are uncertain (1), and reliability is unknown (3). A total score of 5 is given for effectiveness.

Implementability. This technology is well established but may have process development difficulties at the anticipated flow rates (3), space requirements are unknown because reaction parameters are undefined (3), and process-related health and safety considerations are unknown (3). A score of 9 is given for implementability.

Cost. This technology would require significant development costs (1), capital costs are unknown (3); O&M costs are unknown (3). A score of 7 is given for cost.

Acceptance. This technology would likely meet with resistance. A score of 1 is given for acceptance.

The total score for chemical reduction is 22 out of 50.

5.3.11 Alternative A-11: Reduction—Electrochemical Reduction

Electrochemical reduction involves the reduction of perchlorate ion to elemental oxygen and chlorine by contacting the aqueous stream with suitable electrode elements and current. Electrochemical reduction has not been proven to reduce concentrations of perchlorate, and a suitable electrode material has not been identified.

The viability of electrochemical reduction is unclear until a suitable electrode and operating conditions have been identified. Potential disadvantages of electrochemical reduction are the operating costs and formation of hydrogen and oxygen gas at the anode and cathode. Again, any reduction byproducts would have to be harmless for potable water use.

The scoring for electrochemical reduction is as follows:

Effectiveness. The technology's effectiveness for perchlorate is unknown (1), suitable reducing conditions applicable to perchlorate are unknown and therefore effects on human health and the environment are uncertain (3), and reliability is unknown (3). A total score of 7 is given for effectiveness.

Implementability. This technology is well established but will require process development efforts (3), space requirements are unknown because reaction parameters are undefined (3), and process health and safety considerations are unknown (3). A score of 9 is given for implementability.

Cost. This technology would require moderate development costs (3), capital costs would be high (1), and O&M costs are anticipated to be high (1). A score of 5 is given for cost.

Acceptance. This technology would likely encounter moderate scrutiny. A score of 3 is given for acceptance.

The total score for chemical reduction is 24 out of 50.

5.3.12 Alternative A-12: Reduction—Catalyzed Chemical Reduction

Catalyzed chemical reduction involves the reduction of perchlorate ion to elemental oxygen and chlorine by contacting the aqueous stream with a suitable metallic or organic catalyst. Catalyzed chemical reduction has not been proven to reduce perchlorate and a suitable catalyst has not been identified.

The potential disadvantages of catalyzed chemical reduction process are unclear until a suitable catalyst can be identified. Once this is accomplished, optimal reaction conditions need to be developed. There is the potential for pH, temperature, and pressure adjustment, although development efforts would focus on finding a catalyst that operates within standard temperature, pressure, and pH. Again, any reduction byproducts would have to be harmless in potable water.

The scoring for catalyzed chemical reduction is as follows:

Effectiveness. The technology's effectiveness for perchlorate is unknown (1), suitable reducing catalysts applicable to perchlorate are unknown and therefore effects on human health and the environment are uncertain (1), and reliability is unknown (3). A total score of 5 is given for effectiveness.

<u>Implementability</u>. This technology is well established but will require process development efforts (3), space requirements are unknown because reaction parameters are undefined (3), and process-related health and safety considerations are unknown (3). A score of 9 is given for implementability.

<u>Cost</u>. This technology would require significant development costs (1), capital costs are unknown (3), and O&M costs are unknown (3). A score of 7 is given for cost.

<u>Acceptance</u>. This technology would likely encounter moderate scrutiny. A score of 3 is given for acceptance.

The total score for chemical reduction is 24 out of 50.

5.3.13   Alternative A-13:   Reduction—Photocatalytic Reduction

Photocatalytic oxidation through use of a semiconductor photocatalyst (i.e., titanium dioxide) is an emerging water treatment technology for destroying a wide spectrum of organic contaminants in water. The contaminants are photocatalytically oxidized into nontoxic forms, such as simple mineral acids, carbon dioxide, and water. The photocatalytic oxidation process currently requires pretreatment of waste streams containing metals and other inorganic ions that interfere with the photocatalytic process. Typically, this is achieved through use of ion exchange. Photocatalytic oxidation has been used to treat cyanide, an inorganic anion. Currently, the feasibility of photocatalytic oxidation for the treatment of perchlorate is not known. However, because this process has been identified as having the potential to degrade perchlorate, it has been included in this evaluation.

The scoring for photocatalytic oxidation is as follows:

<u>Effectiveness</u> - Photocatalytic oxidation has not been demonstrated to degrade perchlorate ion (1), perchlorate decomposition byproducts are not understood (1), and reliability of technology is not known (1). A total score of 3 is given for effectiveness.

<u>Implementability</u> - Photocatalytic oxidation is a relatively new technology and equipment availability is unknown (1), would require moderate space (1), and has unknown health and safety concerns (3). A total score of 5 would be given for implementability.

Cost - Photocatalytic oxidation would likely require high developmental costs (1), would have relatively high capital costs due to equipment and construction necessities (1), and would have high operating costs due to oxidizer use and electrical consumption (1). A total score of 3 is given for cost.

Acceptance - There is not enough information available to determine whether photocatalytic oxidation would be accepted. A total score of 1 is given for acceptance.

The total score for photocatalytic reduction is 12 out of 50.

5.3.14 Alternative A-14: Precipitation—Chemical Precipitation

Chemical precipitation has been demonstrated to be effective in removing perchlorate ion from water. Chemical precipitation would potentially involve the precipitation of complexed perchlorate ion with perchlorate-specific reagent or through the addition of calcium and alumina precipitating agents (used for nitrate treatment).

The disadvantages of a chemical precipitation process involve adjustment of the influent stream pH, temperature, and pressure and the addition of chemical precipitating compounds. Optimal reaction conditions need to be developed and the effluent stream would have to be treated prior to discharge to adjust pH and remove any precipitating compounds in excess of regulatory standards. The properties of precipitated solids are unknown, and handling may present a safety (explosion) hazard. Precipitated solids will likely require pretreatment prior to disposal.

The scoring for chemical precipitation is as follows:

Effectiveness. The technology's effectiveness for perchlorate is unknown (1), suitable precipitating agents applicable to perchlorate are unknown and therefore effects on human health and the environment are uncertain (1), and reliability is unknown (3). A total score of 5 is given for effectiveness.

Implementability. Precipitation is a well-established technology but is undefined here (3), space requirements are unknown because reaction parameters are undefined (3), and process-related health and safety considerations are unknown (3). A score of 9 is given for implementability.

Cost. This technology would require significant development costs (1), capital costs are unknown (3), and O&M costs are unknown (3). A score of 7 is given for cost.

<u>Acceptance</u>. This technology would likely meet with resistance. A score of 1 is given for acceptance.

The total score for chemical reduction is 22 out of 50.

5.4 Summary

The total scores of each technology screening alternative is summarized in Table 5-3. The six top-ranking technologies are emphasized in bold. From the technology with the highest score to the technology with the sixth highest score, these are biochemical reduction, ion exchange, reverse osmosis, electrodialysis, activated carbon adsorption, and capacitive deionization. These six technologies are carried forward to Section 6.0 for a more detailed evaluation.

The fact that six of these technologies are carried forward does not indicate that all six will be effective or cost effective in treating perchlorate in groundwater or that all six should be considered candidates for bench-scale or pilot-scale testing. This large number of technologies was carried forward to avoid elimination of a technology that may be effective in perchlorate treatment but due to the scoring criteria may not have received a sufficiently high score to have been carried forward.

6.0 CONCEPTUAL DESIGN AND COST EVALUATION

The purpose of this section is to evaluate in more detail each of the six technologies that passed the initial technology screening (Section 5.0). This more detailed evaluation includes development of a conceptual design and cost estimate for each treatment technology. The purpose of developing a conceptual design for each technology was to allow the technology to be described such that the reader could better visualize the treatment process as part of the BPOU project. With a conceptual engineering design available, a cost estimate can then be developed with greater certainty. Based on the initial screening, the following technologies were subjected to this more detailed evaluation.

- Biochemical reduction
- Activated carbon adsorption
- Ion exchange
- Capacitive deionization
- Reverse osmosis
- Electrodialysis

Cost summaries for these technologies are provided in Tables 6-1 through 6-6. Cost estimates were developed based on manufacturer equipment quotations, conceptual treatment design and building layouts, experience on similar projects, typical percentage indices, and published cost data. Costs were adjusted to 1997 values, when necessary, using ENR's *Building Cost Index* or *Construction Cost Index*, as appropriate.

Costs developed as part of this feasibility evaluation are typically accurate to within plus or minus 50 percent. Actual costs will be significantly impacted if actual conditions vary from the assumptions used to develop the cost estimates. The estimates were prepared in accordance with standard engineering practice for estimating preliminary project costs. These estimates were developed for comparative planning purposes, but no guarantee is provided that the proposals, bids, or actual project costs will not vary from the costs presented.

The primary design assumptions used to develop the cost estimates were as follows:

- Design flow rate of 30 million gallons per day (mgd) [20,000 gpm]
- Central treatment plant
- Influent water quality as shown in Table 6-7

- Potable treatment plant effluent
- Treatment and reuse of reject/regeneration waters

Reverse osmosis, ion exchange, and electrodialysis are well-established technologies and include the least uncertainty with respect to cost. Developing costs for biological treatment using GAC/FB is also relatively straightforward based on information available from pilot plant operating experience and design information for the full-scale system planned for Aerojet's Sacramento facility. Capacitive deionization is an emerging technology, and numerous uncertainties exist involving cost of fabricating treatment equipment, proprietary electrochemical materials, and the residence time and associated quantity of material required to achieve optimum treatment performance.

A conceptual design was developed for each treatment technology to estimate treatment costs. The following paragraphs discuss the major design parameters used for each system as well as a description of facilities and equipment common to all of the treatment systems.

Common Facilities and Equipment

Facilities and equipment common to all of the treatment technologies include an administration building, a treatment building, site work, emergency power supply, and chlorination equipment. The administration building, shown in Figure 6-1, includes a supervisor office, records and conference room, and a laboratory. Laboratory equipment was assumed to include an ion chromatograph for measurement of perchlorate at very low detection limits (per EPA Method 300, modified). The treatment building, shown in Figure 6-2, includes a spare parts and maintenance equipment room and chlorination facilities. The chlorination system was designed for a maximum chlorine dose of 4 mg/L, an average dose of 2 mg/L, and includes a chlorine scrubber. Required treatment building area varies for each technology and was estimated based on vendor information and previous experience with similar treatment systems. Building costs were estimated using Mean's Building Cost Data. Chlorination equipment and major laboratory equipment were estimated using vendor budget prices. Site work and emergency power supply were estimated using vendor information and previous experience with similar treatment systems.

Five of the six technologies evaluated are not destructive technologies. These technologies transfer perchlorate from the influent groundwater to another medium (e.g., carbon) or a waste stream (e.g., RO reject water). Because of the significant design capacity of the BPOU project and cost implications of performing offsite treatment of these wastes, treatment of these waste streams will need to occur onsite. Therefore, for all technologies, except biochemical reduction, additional common facilities will be needed

for waste stream treatment. In fact, the technology for waste stream treatment for reverse osmosis, electrodialysis, capacitive deionization, and ion exchange may be biochemical reduction.

6.1   Biochemical Reduction Using GAC/FB

The biochemical reduction treatment system includes methanol and nutrient feed systems, GAC/FB reactors, filter polymer feed systems, multimedia filters, treated water reservoir, distribution pumping system, backwash water storage lagoon and reclamation system, filter backwash system, piping, electrical, and control systems. A conceptual process schematic for the GAC/FB treatment system is shown in Figure 6-3.

The GAC/FB reactors were designed using an overflow rate of 12 gpm/ft^2 and a contact time of 10 minutes. This results in 12 reactors, each 12 feet square and 20 feet high built of concrete using common wall construction. The 12 reactors, each with a treatment capacity ranging between 2.5 and 3.0 mgd, will provide a total finished water treatment capacity of 30 mgd, including spare treatment capacity for maintenance. Approximately 400 tons of GAC is required to fill the reactors. Methanol consumption is estimated at 2,500 gallons per day (gpd), which will require a railroad siding for delivery and a day use chemical storage tank (approximately 5,000 gallons). The nutrient feed systems are relatively small compared to the methanol feed system. Estimated required building area for the GAC/FB system is 5,000 ft^2, and the outside area required for the railroad siding with methanol and nutrient feed systems is estimated at 3,000 ft^2.

High-rate multimedia filters were selected using an overflow rate of 4 gpm/ft^2. This results in 8 filters, each 30 feet long and 25 feet wide built of concrete using common wall construction. The filter aid polymer feed system for the filters includes dry chemical storage, dry chemical feeder, mixing tanks, and feed pumps. The filter backwash system includes a backwash water storage tank, pumps, and aeration equipment. Filter backwash will be stored in an onsite lagoon and reclaimed before being recycled to the plant influent. The reclamation system will consist of activated alumina coagulation, flocculation, and clarification. Solids collected from the clarifier will be dewatered prior to disposal using a plate and frame filter press. Approximately 10 tons of alum sludge will be produced per day, assuming a moisture content of 80 percent. The annual sludge disposal costs are estimated to be $100,000. The estimated building area required for the multimedia filters and associated equipment is 10,000 ft^2, and the onsite storage lagoon will require approximately 1 acre of land.

Water from the GAC/FB system will be collected in a 2-million-gallon underground concrete reservoir prior to delivery using a 30 mgd pumping system.

The GAC/FB treatment system is estimated to achieve 100 percent product water recovery with a perchlorate removal of greater than 95 percent.

O&M costs for the biological treatment system with GAC/FB include site administrative and operating personnel, power, chemicals (methanol, nitrogen, phosphorous, polymer), and replacement GAC.

6.2   Liquid-Phase Granular Activated Carbon

The major components of the GAC treatment system include liquid-phase GAC contactors, activated carbon liquid slurry transport and thermal regeneration systems for the onsite reactivation of perchlorate-saturated GAC, a backwash and water reclamation system for the removal of GAC fines, piping, electrical, and control systems. A conceptual process schematic for the GAC treatment system is shown in Figure 6-4.

For GAC treatment, 11 contactors, each with a treatment capacity of 3.0 mgd, are required to provided a total finished water treatment capacity of 30 mgd. The contactors will be sequentially rotated in and out of service for maintenance or regeneration of the spent GAC. Each contactor will have 20-foot-square dimensions and a GAC bed depth of 10 feet. Approximately 1,200,000 pounds of GAC will be initially required to fill the contactors. The GAC will be installed in open concrete filter basins/contactors and will operate in a gravity downflow, parallel configuration. Each GAC contactor will have an "empty bed contact time" of 12 minutes and a surface hydraulic loading rate of 5.2 gpm/ft^2. The contactors will operate at a constant flow rate, and the hydraulic head required for gravity flow will be contained within each concrete structure with a resulting total contactor sidewall depth of approximately 20 feet. The maximum pressure loss through the gravity GAC contactors is estimated to range between 3 and 4 psi. Product water from the GAC system will be collected in a 2-million-gallon, underground, concrete, treated water reservoir prior to a 30 mgd pumping system delivering the finished water to the municipal water supply at a system pressure ranging between 70 and 90 psi. Total building area required for the treatment system is estimated to be 12,000 ft^2, including the area required for the onsite thermal regeneration of the spent GAC.

Spent GAC will be thermally regenerated onsite, and the bed life of the GAC has been estimated at 7 days. GAC will be hydraulically transported to and from thermal regeneration in a liquid slurry phase. After regeneration and reinstallation of GAC in a contactor, the GAC will be backwashed to remove carbon fines created during the regeneration and transport process. The cost estimate assumes that at least 10 percent of the total GAC volume will be "lost" as fines during each regeneration cycle. The backwash and

regeneration water will be reclaimed using a 500,000-gallon storage tank and an ultrafiltration membrane system to separate the carbon fines from the water. Carbon fines will be dewatered using a plate and frame filter press, and the carbon fines will be disposed of as nonhazardous waste at an approved landfill. Based on 52 regeneration cycles for 10 contactors each year, approximately 6,400,000 pounds of new GAC will be required annually to replace carbon fines. The annual cost of carbon fines disposal is estimated to be approximately $120,000 based on a solids content of 35 percent. The frequency of carbon changeout presents a materials handling challenge as commercial operations do not change out carbon this frequently.

The GAC system is estimated to achieve 100 percent product water recovery with a perchlorate removal of greater than 90 percent. The perchlorate treatment removal efficiency is based on a preliminary estimate from isotherm data, and pilot-scale treatability studies are recommended to verify the estimated performance and the frequency of GAC regeneration.

O&M costs for the GAC treatment system include site administrative and operating personnel, power, GAC, thermal regeneration systems, water reclamation systems, carbon fines disposal costs, and an estimated regeneration of the GAC every week.

6.3   Ion Exchange

The major components of the ion exchange treatment system include cartridge filters, ion exchange pressure vessels (contactors), chemical feed systems for the rinsing and regeneration of the ion exchange media, piping, electrical, and control systems. In addition, a biological GAC/FB treatment system will be used to remove perchlorate from the regeneration flows produced during the restoration of the ion exchange resin. A conceptual process schematic for the ion exchange treatment system is shown in Figure 6-5.

For ion exchange treatment, 28 contactors, each with a treatment capacity of 1.2 mgd, are required to provided a total finished water treatment capacity of 30 mgd. Three of the contactors will be sequentially rotated into and out of service for maintenance or regeneration of the ion exchange resin. Each contactor will have a 12-foot diameter and a sidewall height of approximately 8 feet. The contactors will be installed in a downflow, parallel operating configuration. Influent water will be pumped directly through cartridge filters for removal of any suspended solids prior to the contactors. The operating pressure of the contactors is estimated to range between 80 and 100 psi. This operating pressure is based on the treated water from the contactors being delivered directly into the municipal water supply, without the necessity of constructing a treated water storage reservoir and pumping system. Chemical feed systems used to

regenerate the ion exchange resin include a sodium chloride regenerate solutions and the associated metering pumps, piping, and chemical storage tanks. Total building area required for the treatment system is estimated to be 15,000 ft^2, including the area required for the treatment of the ion exchange regeneration wastewaters.

The ion exchange treatment system is estimated to achieve 85 percent water recovery with a perchlorate removal of greater than 95 percent. The perchlorate treatment removal efficiency is based on a preliminary estimate by ion exchange resin manufacturers.

Ion exchange resin manufacturers have initially indicated that a Type I chloride resin will most likely be the optimum resin for removing low concentrations of perchlorate from groundwater and meeting the treatment objectives. The ion exchange manufacturers also believe that pH adjustment of the influent water (and readjustment of the effluent water) will not be necessary to achieve satisfactory treatment performance since the influent perchlorate concentrations are relatively low (100 μg/L). This recommendation differs from recent ion exchange treatability data for groundwater with perchlorate concentrations that are several orders of magnitude higher in concentration. For estimating purposes, no pH adjustment will be included.

This technology concentrates perchlorate and other anions into a saline waste brine. Initial pilot-scale work at Aerojet's Sacramento facility suggests that this brine may contain up to 3,000 mg/L perchlorate. Treatment and disposal alternatives for the ion exchange rinse flows produced during the regeneration of the ion exchange media are described in Section 6.7.

The cost estimate, however, is based on the optimistic assumptions and preliminary estimates provided by the ion exchange resin manufacturers, and if pH adjustment is necessary, capital and operating costs will increase.

O&M costs for the ion exchange system include site administrative and operating personnel, power, and operation of resin regeneration systems.

6.4   Capacitive Deionization

The major components of the CDI treatment system include carbon aerogel electrochemical cells/stacks, treated water reservoir, distribution pumping system, CDI cleaning system, piping, electrical, and control systems. In addition, a biological GAC/FB treatment system will be used to remove perchlorate from the

regeneration flows produced during the restoration of the carbon-aerogel material. A conceptual process schematic for the CDI treatment system is shown in Figure 6-6.

Based on information from the manufacturer and reports by independent researchers for the newly emerging technology, it is estimated that between 0.5 and 12 ft^2 of carbon-aerogel per gallon per day will be required to meet the treatment objectives for the removal of perchlorate. The cost estimate is based on an assumed material loading rate of 1 ft^2 of carbon aerogel per gallon per day, and this preliminary, and optimistic, loading rate should be verified through pilot testing if this technology is to be carried forward. The electrochemical cells will be installed in a parallel operating configuration. No influent pumping system is assumed to be needed since the influent groundwater supply could meet the hydraulic pressure demands of the CDI treatment system. Product water from the CDI system will be collected in a 2-million-gallon, underground, concrete, treated water reservoir prior to a 30 mgd pumping system delivering the finished water to the municipal water supply at a system pressure ranging between 70 and 90 psi. No full-scale facility has been constructed using this technology; however, based on information from the manufacturer, a 30 mgd treatment plant is assumed to require a treatment building of approximately 40,000 ft^2, including the area required for the GAC/FB treatment of the concentrated wastewaters.

One of the primary reasons that no large-scale CDI treatment system has been constructed is that, in the past, the carbon aerogel was cost prohibitive at $16.00/ft^2. The manufacturer, however, has indicated that recent innovations have decreased the cost of manufacturing carbon aerogel treatment units to approximately $1.80/ft^2 and anticipates further reductions in the near future. The cost estimate here was based on this estimate from the manufacturer. This magnitude of cost reduction should be considered skeptically until the manufacturer can provide documentation or assurances that this lower cost can be realized. If the BPOU Central Treatment Plant is to be the first large-scale CDI water production facility to be constructed, the costs should be reexamined in greater detail.

CDI is estimated to achieve greater than 95 percent water recovery with a perchlorate removal of greater than 95 percent. The perchlorate treatment removal efficiency is based on a preliminary estimate by the manufacturer.

This technology is not destructive and merely transfers perchlorate from the influent groundwater to a concentrated waste stream that in turn needs treatment. Treatment and disposal alternatives for the wastewater rinse flows produced during the regeneration of the CDI electrochemical cells are described in Section 6.7.

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O&M costs for the CDI treatment system include site administrative and operating personnel, power, and the electrochemical cell regeneration systems.

6.5   Reverse Osmosis

The major components of the reverse osmosis treatment system include cartridge filters, chemical feed systems for pretreatment, high-pressure feed pumps, membrane elements and pressure vessels, chemical feed systems for post-treatment, degasifiers, treated water reservoir, distribution pumping system, membrane cleaning system, piping, electrical, and control systems. In addition, a biological GAC/FB treatment system will be used to remove perchlorate from the brine flows rejected by the reverse osmosis system. A conceptual process schematic for the reverse osmosis treatment system is shown in Figure 6-7.

For reverse osmosis treatment, 11 treatment trains each with a treatment capacity of 3.5 mgd are required to provide a total finished water treatment capacity of 30 mgd. One of the treatment trains will be sequentially rotated into and out of service for maintenance. Each treatment train will contain 78 pressure vessels (52 first-stage vessels and 26 second-stage vessels), and each pressure vessel contains 6 membrane elements. The operating pressure of the reverse osmosis system is estimated to range between 150 and 200 psi. The dimensions of each treatment train are approximately 25 feet long, 10 feet wide, and 10 feet high. Chemical feed systems include pretreatment pH adjustment (sulfuric acid), antiscalant, and post-treatment pH adjustment (caustic soda), and associated metering pumps, piping, and chemical storage tanks. Product water from the reverse osmosis system would require a 2-million-gallon, underground, concrete, treated water reservoir prior to a 30 mgd pumping system delivering the finished water to the municipal water supply at a system pressure ranging between 70 and 90 psi. Total building area required for the treatment system is estimated to be 35,000 ft^2, including the area required for the treatment of the brine flows.

The reverse osmosis treatment system is estimated to achieve 85 percent product water recovery with a perchlorate removal of greater than 95 percent. The perchlorate treatment removal efficiency is based on a preliminary estimate by membrane manufacturers.

This technology is not destructive but concentrates perchlorate in a saline reject water. This reject water would need to be treated prior to blending with the effluent water from the treatment plant or discharge to a brine line. Treatment and disposal alternatives for the brine flows rejected by the reverse osmosis treatment system are described in Section 6.7.

O&M costs for the reverse osmosis system include site administrative and operating personnel, power, pre- and post-treatment chemicals, membrane replacement (every 5 years), and an estimated replacement of the cartridge filters every 2 weeks.

6.6   Electrodialysis

The major components of the ED treatment system include cartridge filters, ED membranes/vessels/stacks, treated water reservoir, distribution pumping system, ED stack cleaning system, piping, electrical, and control systems. In addition, a biological GAC/FB treatment system will be used to remove perchlorate from the brine flows rejected by the ED system. A conceptual process schematic for the ED treatment system is shown in Figure 6-8.

For ED treatment, 26 treatment trains each with a treatment capacity of 1.25 mgd are required to provide a total finished water treatment capacity of 30 mgd. Two of the treatment trains will be sequentially rotated into and out of service for maintenance. Each treatment train contains ion selective membrane stacks, hydraulic controls, electrodes, and the associated electrical power equipment. The operating pressure of the ED system is estimated to range between 5 and 10 psi, and no influent pumping system is assumed to be needed since the influent groundwater supply pumping system could meet the hydraulic pressure demands of the ED system. The dimensions of each ED treatment train are approximately 55 feet long, 18 feet wide, and 10 feet high. Product water from the ED system will be collected in a 2-million-gallon, underground, concrete, treated water reservoir prior to a 30 mgd pumping system delivering the finished water to the municipal water supply at a system pressure ranging between 70 and 90 psi. Total building area required for the treatment system is estimated to be 65,000 ft^2, including the area required for the treatment of the brine flows.

The ED treatment system is estimated to achieve 90 percent product water recovery with a perchlorate removal of greater than 95 percent. The perchlorate treatment removal efficiency is based on a preliminary estimate by an ED manufacturer.

Like reverse osmosis, electrodialysis is not a destructive technology and produces a saline waste stream that requires treatment. Treatment and disposal alternatives for the brine flows rejected by the ED treatment system are described in Section 6.7.

O&M costs for the electrodialysis system include site administrative and operating personnel, power, cleaning chemicals, and ED membrane replacement (every 10 years).

6.7 Brine Treatment

Four of the five treatment processes subjected to a detailed technical and cost evaluation do not effect destruction of the perchlorate ion. Only the GAC/FB process alters the perchlorate ion. Activated carbon requires onsite regeneration due to the frequency of carbon changeout. All other technologies remove perchlorate but concentrate it in a waste stream. Both reverse osmosis and electrodialysis technologies reject saline brines. Ion exchange produces saline waste regeneration solution. Capacitive deionization also produces a saline waste stream. It has been estimated that ion exchange, capacitive deionization, reverse osmosis, and electrodialysis will produce waste streams comprising 15, 5, 15, and 10 percent of the original influent volume, respectively.

There are three options for these saline solutions:

- Solutions could be directly discharged to the San Gabriel Basin brine line without treatment and discharged to the ocean.

- Solutions could be pretreated using a GAC/FB process as depicted on Figure 6-9 to reduce perchlorate concentrations prior to ocean discharge via the brine line.

- Solutions could be treated to remove perchlorate using GAC/FB technology and resultant brines blended back into the delivery stream.

It is unlikely that untreated discharge to the ocean will be acceptable. In addition, if a untreated or treated brine is discharged to the ocean, the resultant treated water to be delivered to local and regional water purveyors will have very low dissolved solids with little buffer capacity. The water will therefore be corrosive and tasteless.

If treated brine cannot be blended back into the delivery stream, the effluent from the treatment plant should be blended with other water to restore buffer capacity.

If direct discharge of saline solutions to the brine line is performed, the capital and operating costs for the project will decrease by $5 million and $1 million, respectively. The brine discharge pipeline is estimated to be approximately 1-mile in length from the treatment site and would have a capital cost of approximately $0.5 million. It is assumed that there will be no operating costs to discharge the brine flows to the regional disposal pipeline. Also, if brine flows are not reclaimed, the total volume of finished water produced by the treatment facility will decrease by approximately 15 percent (4.5 mgd) for the reverse osmosis and ion exchange treatment systems and 10 percent (3 mgd) for the ED and CDI treatment

systems. The cost to the project due to lost water sales is significant but has not been taken into consideration for this analysis.

For purposes of comparative cost analysis, it has been assumed that brine flows containing the concentrated salts, metals, perchlorate, and nitrate rejected by the reverse osmosis membranes, ED treatment system, and CDI system and contained in the rinse waters from the ion exchange system will be treated by a biological GAC/FB system to remove the nitrates and perchlorate. Brine flows will be equalized and stored in a 1-million-gallon reservoir prior to pumping through the brine treatment system. The biological GAC/FB brine treatment system will consist of two GAC/FB reactors using an overflow rate of 12 gpm/ft^2 and a contact time of 10 minutes. The reactors will be 12 feet square and 20 feet high built of concrete using common wall construction. Approximately 70 tons of GAC will be used as the support medium for biological growth. Assuming greater than 95 percent biological removal of the concentrated nitrate and perchlorate, the methanol consumption is estimated at 2,000 gpd, which will require a railroad siding for delivery and a daily use transfer storage tank (approximately 5,000 gallons). The nutrient feed systems are relatively small compared to the methanol feed system. Estimated required building area for the GAC/FB system and associated multimedia filters is 5,000 ft^2, and the outside area required for the railroad siding with methanol and nutrient feed systems is estimated at 3,000 ft^2.

After biological treatment, suspended solids will be removed from the brine flows using high-rate multimedia filters. The multimedia filters are based on an overflow rate of 4 gpm/ft^2. This results in two filters, each 20 feet square and built of concrete using common wall construction. The polymer feed system for the filters includes dry chemical storage, dry chemical feeder, mixing tanks, and feed pumps. The filter backwash system includes a backwash water storage tank, pumps, and air scour aeration equipment. Filter backwash will be stored in an onsite lagoon and will be reclaimed before being recycled to the plant influent. The reclamation system will consist of activated alumina coagulation, flocculation, and clarification. Solids collected from the clarifier will be dewatered prior to disposal using a plate and frame filter press. Approximately 1 to 2 tons of alum sludge will be produced per day, assuming a moisture content of 80 percent. The annual sludge disposal costs are estimated to be $15,000. Brine flows treated through the biological GAC/FB and multimedia filters will be recombined with water produced by either the reverse osmosis system, ion exchange system, CDI system, or the ED system in the finished water storage reservoir or the piping connection to the distribution system.

The treatment system described above will treat all of the influent water with no liquid discharge of brine flows or other wastewaters.

O&M costs for the brine recovery treatment system include administrative and operating personnel, power, nutrients, replacement GAC, other treatment chemicals, and sludge disposal.

6.8   Comparative Capital and Operating Costs

Total construction cost includes costs for the treatment system and all facilities. The total capital cost includes contingencies at 20 percent of total construction and engineering costs, and administration at 20 percent of total construction cost. Budgetary equipment and O&M costs were obtained, where possible, from equipment manufacturers. Each manufacturer was supplied with the water quality data shown in Table 6-7 and the design assumptions outlined above. In the absence of manufacturer information, previous experience and standard engineering design and cost estimating practices were used to estimate costs. Total capital costs were amortized over 20 years using 8 percent financing and added to annual O&M costs to obtain a total annual treatment cost for each technology in 1997 dollars (Table 6-8).

Biological treatment with GAC/FB is the lowest-cost treatment alternative with an estimated total annual treatment cost of $6.6 million. The remaining treatment alternatives, in order of increasing total annual treatment costs, are ion exchange, electrodialysis, reverse osmosis, capacitive deionization, and activated carbon adsorption. Total annual treatment costs for these alternatives are approximately 1.6, 2.1, 2.5, 2.5, and 3.1 times greater, respectively, than that for biological treatment.

7.0 RECOMMENDATIONS AND PROPOSED ACTIVITIES

This evaluation has identified six technologies that have strong potential for effectively removing the perchlorate ion from groundwater. These technologies are:

- Biochemical reduction
- Activated carbon
- Ion exchange
- Capacitive deionization
- Electrodialysis
- Reverse osmosis

These technologies have been developed and tested to varying levels with respect to the removal of perchlorate. Therefore, our knowledge of the effectiveness, implementability, acceptance, and cost varies with each technology.

To make an informed decision regarding which technology is best suited to be used on the BPOU project, additional studies are necessary. The purpose of these studies is to raise the level of knowledge of each technology to a point where it can be compared with the other viable technologies, or to identify a factor or factors that make the technology unattractive for further consideration. Technology characteristics that would prevent further consideration of the technology could be related to effectiveness, implementability, acceptance, or cost.

Plans for further evaluation of each technology are described below.

7.1   Biochemical Reduction

Phase 1 pilot-scale testing of biochemical reduction is underway at Aerojet's Sacramento facility. Previous studies have demonstrated the effectiveness of this technology, and results from Phase 1 pilot testing will confirm these results for San Gabriel Basin effluent objectives. In addition, Aerojet is at the 60 percent design stage on a 1,500 gpm full-scale treatment system using this same technology as part of its GET-F groundwater extraction and treatment system. Design and construction of the full-scale system in Sacramento will provide data on implementability and cost.

Because studies are underway to further test this technology, no additional work is planned. Details of Phase 1 treatability testing and a conceptual approach for Phase 2 treatability testing can be found in HLA 1997a and 1997c.

7.2 Activated Carbon

GAC has been shown to be effective at adsorbing perchlorate and is continuing to undergo testing by several vendors/manufacturers. Current data suggests, however, that adsorption of perchlorate by GAC is weak, the perchlorate once adsorbed is easily displaced, and that GAC breakthrough is extremely rapid. Therefore, changeout/regeneration will be needed so frequently that materials handling will be complex and costs will be prohibitive. As described in Section 6.2 and presented in Table 6-2, annual operations and maintenance are estimated to be approximately $16 million. For this reason, GAC has been eliminated from further consideration.

7.3 Ion Exchange

Aerojet has already performed considerable work to evaluate the effectiveness of ion exchange as a perchlorate treatment technology. Bench-scale laboratory testing has been performed in Sacramento. Various resins were tested and a preferred resin selected. Testing using this resin proved that an effluent concentration less than the 400 μg/L reporting limit was possible. The resin was successfully regenerated. Waste regenerant was further concentrated using electrodialysis to less than 1 percent of the original influent volume, containing 3,000 mg/L of perchlorate. The perchlorate was successfully reduced using biochemical reduction technology.

Additional bench-scale testing to ensure ion exchange technology can achieve potability standards would be needed to implement this technology on the BPOU project. The BPOUSC recently learned that the Montgomery Watson Laboratory in Pasadena, California, is performing or is planning bench-scale testing of ion exchange technology specifically for application with perchlorate removal. The BPOUSC recommends that it provide input and guidance to Montgomery Watson efforts and receive results of bench-scale ion exchange testing in trade for sharing performance information for biochemical reduction technology.

Behind biochemical reduction, ion exchange is clearly the second most cost-effective technology available for treatment of groundwaters containing perchlorate. Although pilot-scale testing may be warranted at a later date, at this time further processing and interpretation of available bench-scale information and bench-scale testing to confirm that this technology will produce potable water is recommended.

7.4   Capacitive Deionization

Capacitive deionization is considered to be an attractive candidate technology from the standpoint of low annual cost for operations and maintenance. There is, however, little information available on its performance with respect to perchlorate removal, and initial estimates of capital cost are generally greater than for other technologies considered.

Although the technology has the potential to be viable, current information suggests that it may not be cost effective. The BPOUSC therefore recommends that it continue to maintain a dialog with the vendor, requesting performance and cost information as it becomes available. If the vendor can provide adequate performance data and demonstrate that design and construction of a full-scale system can be cost effective, this technology will be considered further. If, however, these data are not forthcoming, the technology will be eliminated from consideration.

7.5   Reverse Osmosis

Reverse osmosis has proven successful in removing ions of all types from water. Although this technology has not been directly tested for application in perchlorate removal, it is a widely accepted method for removing dissolved substances from water, it is known to be implementable, and a significant volume of information to allow cost projections is available. Therefore, the information needed to complete the comparative evaluation of reverse osmosis against other candidate technologies includes performance related to perchlorate removal and operational considerations that may be related to perchlorate treatment. One significant operation consideration is selection of a method for treatment of reject brine and the cost associated with this brine treatment.

The BPOUSC will contact vendors of this technology that are gathering additional information on implementability and cost. The BPOUSC will seek to identify a vendor that will perform bench-scale testing for perchlorate. Should a vendor be willing to provide performance information, this technology can be reconsidered.

7.6   Electrodialysis

Although sufficient information exists on the effectiveness of electrodialysis in removing perchlorate from solution, there is a lack of information on the performance of this technology at concentrations that will be encountered in the San Gabriel Basin. It has not been demonstrated that electrodialysis can effectively meet potability requirements. As this technology is not destructive, treatment and disposal of saline

wastes must be performed. As the cost of this technology is clearly higher than either biochemical reduction or ion exchange, additional effort on the part of the BPOUSC is not recommended.

The BPOUSC will contact vendors of this technology that are gathering additional information on implementability and cost. The BPOUSC will seek to identify a vendor that will perform bench-scale testing for perchlorate. Should a vendor be willing to provide performance information, this technology can be reconsidered.

Table 3-1

Physical and Chemical Properties of Perchlorate Salts

Physical or Chemical Property	Ammonium Perchlorate	Sodium Perchlorate	Perchloric Acid	Potassium Perchlorate
Formula	NH_4ClO_4 [1]	$NaClO_4$	$HClO_4$	$KClO_4$
Description	odor less white granular crystals	white rhombohedral crystals	colorless oily liquid	colorless crystals or white, crystalline powder
Molecular Weight	117.49 g/mole [1]	122.44 g/mole	100.47 g/mole	138.55 g/mole
Specific Gravity	1.95 g/l [1]	2.02 g/L	1.768 g/L @ 22°C	2.52 g/L
Solubility in Water:	Soluble in water: 10.74 g/100 cc at 0 degrees Celsius [1] 42.45 g/100 cc at 85 degrees Celsius [1]	209 g/100 cc @ 15°C 284 g/100 cc @ 50°C	Miscible in cold water	Soluble in 65 parts cold water Soluble in 15 parts boiling water
Solubility in Other Solvents:	Soluble in acetone [1] Slightly soluble in ethanol [1] Soluble in Methanol [1] Almost insoluble in ether and ethyl acetate [1]	Soluble in alcohol	No data	Insoluble in ether practically insoluble in alcohol
Decomposition Temperature	>150 degrees F; (>66 degrees C) (Explodes at higher temperatures. Stable below these temperatures) [2]	@ 482°C	occurs when distilled at atmospheric pressure	@ 400°C
Melting Point	450°C	130°C	112°C	-610°C

[#]   Reference numbers are provided in brackets
1   Hazardous Substances Data Bank (HSDB) for ammonium perchlorate.
        Printed from the National Library of Medicine. September 8, 1997.
2   MSDS for ammonium perchlorate.   From: http://www.skylighter.com/msds/ammonium_perchlorate.txt

Table 4-1

Selectivity of Modified Cellulose Acetate Membrane to Several Solutes*

Solute	Concentration, moles/liter	Water flux, g./sq. cm.-sec.	Rejection, %	Apparent water permeability p_1, g./cm.-sec.	Apparent solute permeability p_2, cm.-sec.
NaCl	0.90	7.2×10^{-4}	98.1	2.6×10^{-7}	2.0×10^{-10}
NaBr	0.51	6.9×10^{-4}	98.0	1.9×10^{-7}	3.1×10^{-10}
KCl	0.71	7.4×10^{-4}	95.8	2.2×10^{-7}	5.3×10^{-10}
$NaNO_3$	0.029	1.2×10^{-3}	90.1	2.6×10^{-7}	1.9×10^{-9}
$NaClO_4$	0.43	1.1×10^{-3}	86.3	2.3×10^{-7}	2.9×10^{-7}
NH_4ClO_4	0.45	8.5×10^{-4}	77.4	2.1×10^{-7}	5.0×10^{-8}
NH_4NO_3	0.031	1.3×10^{-3}	80.3	2.8×10^{-7}	4.7×10^{-9}
$CaCl_2$	0.47	6.7×10^{-4}	99.1	2.1×10^{-7}	5.3×10^{-10}
Na_2SO_4	0.37	6.2×10^{-4}	99.3	1.6×10^{-7}	1.0×10^{-10}
HNO_3**	0.040	1.3×10^{-3}	51.3	2.7×10^{-7}	1.8×10^{-8}
NH_4OH**	0.050	1.4×10^{-3}	6.2	2.9×10^{-7}	3.0×10^{-7}
Sodium lauryl sulfate	0.0043	1.8×10^{-3}	98.2	3.8×10^{-7}	1.1×10^{-10}
Sucrose	0.15	1.5×10^{-3}	99.7	3.4×10^{-7}	5.0×10^{-11}
Tetramethyl ammonium chloride	0.48	8.9×10^{-4}	99.6	2.5×10^{-7}	5.0×10^{-11}
Tetraethyl ammonium chloride	0.32	1.1×10^{-3}	99.4	2.7×10^{-7}	1.0×10^{-10}

Pressure 102 atm.
Acetyl content of the membrane = 39.8 per cent.
Effective membrane thickness = 0.16
* Perry, Robert H. and Cecil H. Chilton. 1973. Chemical Engineers' Handbook.
** This test was conducted at approximately 0°C to reduce chemical attack. Nevertheless, some loss in selectivity to NaCl occurred during the test.

Table 5-1. Technology Screening Model				
Factor			**Description**	**Maximum Score**
Effectiveness	Effectiveness in treating perchlorate so that effluent is potable		Technologies proven in achieving treatment, protection, or reliability goals are ranked 5; technologies where the data are uncertain or further study is necessary are ranked 3; if current data are unfavorable a rank of 1 is assigned.	5
	Protective of human health and the environment			5
	Reliability			5
Implementability	Established as a water treatment technology, easily implemented within the project schedule		Established, easily implementable technologies with modest space requirements and minimal safety considerations are ranked 5; technologies where data are uncertain or moderate engineering controls are necessary are ranked 3; if current data are unfavorable or significant engineering controls are necessary a rank of 1 is assigned.	5
	Space and layout requirements			5
	Health and safety considerations			5
Cost	Development		Technologies where development, capital, and operation and maintenance (O&M) costs are minimal are ranked 5; technologies where data is uncertain or moderate costs are projected are ranked 3; if cost projections are unfavorable a rank of 1 is assigned.	5
	Capital			5
	Operation and Maintenance			5
Acceptance			Technologies where regulatory, public, and water purveyor acceptance is readily anticipated are ranked 5; technologies that unproven or where concerns are anticipated are ranked 3; technologies where opposition is anticipated are ranked 1.	5
			Total Possible Score:	50

Table 5-2. Technology Screening Alternatives		
Alternative Number	**Technology Classification**	**Technology Description**
A-1	Biological	Biochemical reduction
A-2	Adsorption	Activated carbon
A-3		Ion exchange
A-4		Capacitive deionization
A-5	Liquid extraction	Gettering with reversibly dispirsible carrier
A-6	Membrane technology	Reverse osmosis
A-7		Electrodialysis
A-8	Chemical oxidation/ reduction	Chemical oxidation
A-9		Supercritical water oxidation
A-10		Chemical reduction
A-11		Electrochemical reduction
A-12		Catalyzed chemical reduction
A-13		Photocatalytic Reduction
A-14	Chemical precipitation	Chemical precipitation

Table 5-3
Summary of Technology Screening Alternatives Scores

Alternative Number	Technology	Effectiveness	Implementability	Cost	Acceptance	Total Score (out of 50)
A-1	Biochemical Reduction	13	15	15	3	46
A-2	Activated Carbon	11	9	7	3	30
A-3	Ion Exchange	13	13	13	5	44
A-4	Capacitative Deionization	11	7	9	3	30
A-5	Gettering with Reversibly Dispirsable Carriers	3	5	7	1	16
A-6	Reverse Osmosis	13	13	9	5	40
A-7	Electrodialysis	11	15	9	5	40
A-8	Chemical Oxidation	7	11	3	5	26
A-9	Supercritical Water Oxidation	9	3	3	3	18
A-10	Chemical Reduction	5	9	7	1	22
A-11	Electrochemical Reduction	7	9	5	3	24
A-12	Catalyzed Chemical Reduction	5	9	7	3	24
A-13	Photocatalytic Reduction	3	5	3	1	12
A-14	Chemical Precipitation	5	9	7	1	22

Detailed cost analyses will be presented in Section 6 for the six top-ranking technologies identified in bold type above

Table 6-1

Treatment Costs for Perchlorate Removal by Biological GAC/FB

Capital Cost ($ Million)	
Perchlorate Treatment System	19.0
Facilities (buildings, site work, utilities, etc.)	5.0
Contingencies @ 20%	5.0
Total Construction Cost	*29.0*
Engineering and Administration @ 20%	6.0
Total Capital Cost	*35.0*
O&M Cost ($ Million)	
Annual O&M Cost	3.0
Capital Recovery (20 years @ 8%)	3.6
Total Annual Cost	*6.6*

Notes: 1. All costs are in 1997 dollars.
2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
3. Cost of land and related environmental requirements are not included.

Table 6-2

Treatment Costs for Perchlorate Removal by Granular Activated Carbon

Capital Cost ($ Million)	
Perchlorate Treatment System	20.0
GAC Thermal Regeneration System	7.0
Facilities (buildings, site work, utilities, etc.)	5.0
Contingencies @ 20%	6.0
Total Construction Cost	*38.0*
Engineering and Administration @ 20%	8.0
Total Capital Cost	*46.0*
O&M Cost ($ Million)	
Annual O&M Cost	16.0
Capital Recovery (20 years @ 8%)	4.7
Total Annual Cost	*20.7*

Notes: 1. All costs are in 1997 dollars.
2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
3. Cost of land and related environmental requirements are not included.

Table 6-3

Treatment Costs for Perchlorate Removal by Ion Exchange

Capital Cost ($ Million)	
Perchlorate Treatment System	23.0
Brine Treatment System	5.0
Facilities (buildings, site work, utilities, etc.)	5.0
Contingencies @ 20%	7.0
Total Construction Cost	*40.0*
Engineering and Administration @ 20%	8.0
Total Capital Cost	*48.0*
O&M Cost ($ Million)	
Annual O&M Cost	5.5
Capital Recovery (20 years @ 8%)	4.9
Total Annual Cost	*10.4*

Notes: 1. All costs are in 1997 dollars.
2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
3. Cost of land and related environmental requirements are not included.

Table 6-4

Treatment Costs for Perchlorate Removal by Capacitive Deionization

Capital Cost ($ Million)	
Perchlorate Treatment System	80.0
Brine Treatment System	4.0
Facilities (buildings, site work, utilities, etc.)	7.0
Contingencies @ 20%	18.0
Total Construction Cost	*109.0*
Engineering and Administration @ 20%	22.0
Total Capital Cost	*131.0*
O&M Cost ($ Million)	
Annual O&M Cost	3.0
Capital Recovery (20 years @ 8%)	13.3
Total Annual Cost	*16.6*

Notes: 1. All costs are in 1997 dollars.
2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
3. Cost of land and related environmental requirements are not included.

Table 6-5

Treatment Costs for Perchlorate Removal by Reverse Osmosis

Capital Cost ($ Million)	
Perchlorate Treatment System	34.0
Brine Treatment System	5.0
Facilities (buildings, site work, utilities, etc.)	6.0
Contingencies @ 20%	9.0
Total Estimated Construction Cost	54.0
Engineering and Administration @ 20%	11.0
Total Capital Cost	*65.0*
O&M Cost ($ Million)	
Annual O&M Cost	10.0
Capital Recovery (20 years @ 8%)	6.6
Total Annual Cost	*16.6*

Notes: 1. All costs are in 1997 dollars.
2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
3. Cost of land and related environmental requirements are not included.

Table 6-6

Treatment Costs for Perchlorate Removal by Electrodialysis

Capital Cost ($ Million)	
Perchlorate Treatment System	45.0
Brine Treatment System	5.0
Facilities (buildings, site work, utilities, etc.)	8.0
Contingencies @ 20%	12.0
Total Construction Cost	*70.0*
Engineering and Administration @ 20%	14.0
Total Capital Cost	*84.0*
O&M Cost ($ Million)	
Annual O&M Cost	5.0
Capital Recovery (20 years @ 8%)	8.6
Total Annual Cost	*13.6*

Notes: 1. All costs are in 1997 dollars.
      2. All costs are order-of-magnitude only accurate to within plus or minus 50%.
      3. Cost of land and related environmental requirements are not included.

Table 6-7

Influent Water Quality Parameters Used for Cost Estimating

Parameter	Unit	Average	Maximum
Total Dissolved Solids	mg/L	360	540
Alkalinity	mg/L as $CaCO_3$	180	230
Hardness	mg/L as $CaCO_3$	220	320
Perchlorate	µg/L	50	100
Nitrate	mg/L as N	10	20
Iron	mg/L	0.1	0.5
Manganese	mg/L	0.02	0.05
Copper	mg/L	0.004	0.03
Sulfate	mg/L	33	50
Calcium	mg/L	70	100
Potassium	mg/L	3	4
Magnesium	mg/L	11	18
Chloride	mg/L	20	40

From "Draft Technical Memorandum, Treatment Process Evaluation, Conjunctive Use Feasibility Study, San Gabriel Basin", CH2MHill, September, 1990.

Table 6-8

Summary of Cost Estimates

Treatment Method	Total Capital Cost ($Million)	Annual O&M Cost ($Million)	Total Annual Treatment Cost ($Million)	Total Annual Treatment Cost ($/kgal)	Normalized Treatment Cost
Biological with GAC/FB	35	3.0	6.6	0.60	1.0
Ion Exchange	28	5.5	10.4	0.95	1.6
Liquid Phase GAC	46	16.0	20.7	1.88	3.1
Electrodialysis	84	5.0	13.6	1.06	2.1
Reverse Osmosis	65	10.0	16.6	1.52	2.5
Capacitive Deionization	131	3.0	16.6	1.52	2.5

Notes:
1. Total annual treatment cost determined by adding annual O&M cost and total capital cost amortized over 20 years at 8%.
2. All costs are in 1997 dollars.
3. All costs are order-of-magnitude only accurate to within plus or minus 50 percent.
4. Cost of land and related environmental requirements are not included.

FIGURES
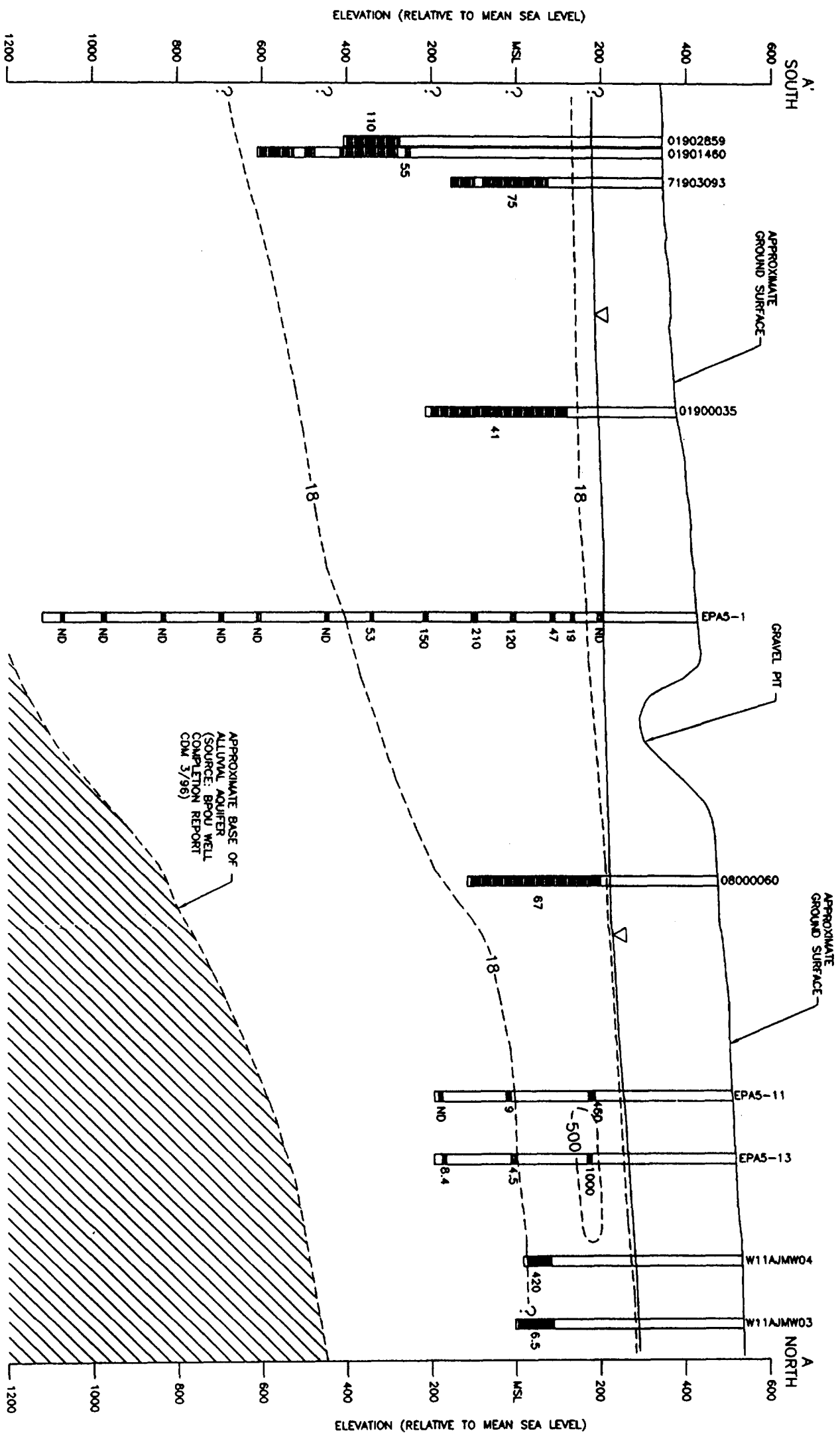
VERTICAL DISTRIBUTION OF
PERCHLORATE CROSS SECTION
JUNE 1997
Baldwin Park Operable Unit
Baldwin Park, California

Harding Lawson Associates
Engineering and
Environmental Services

DRAWN: RLB
JOB NUMBER: 37087.2.3.2
APPROVED:
DATE: 7/97
REVISED DATE:

FIGURE
1-2
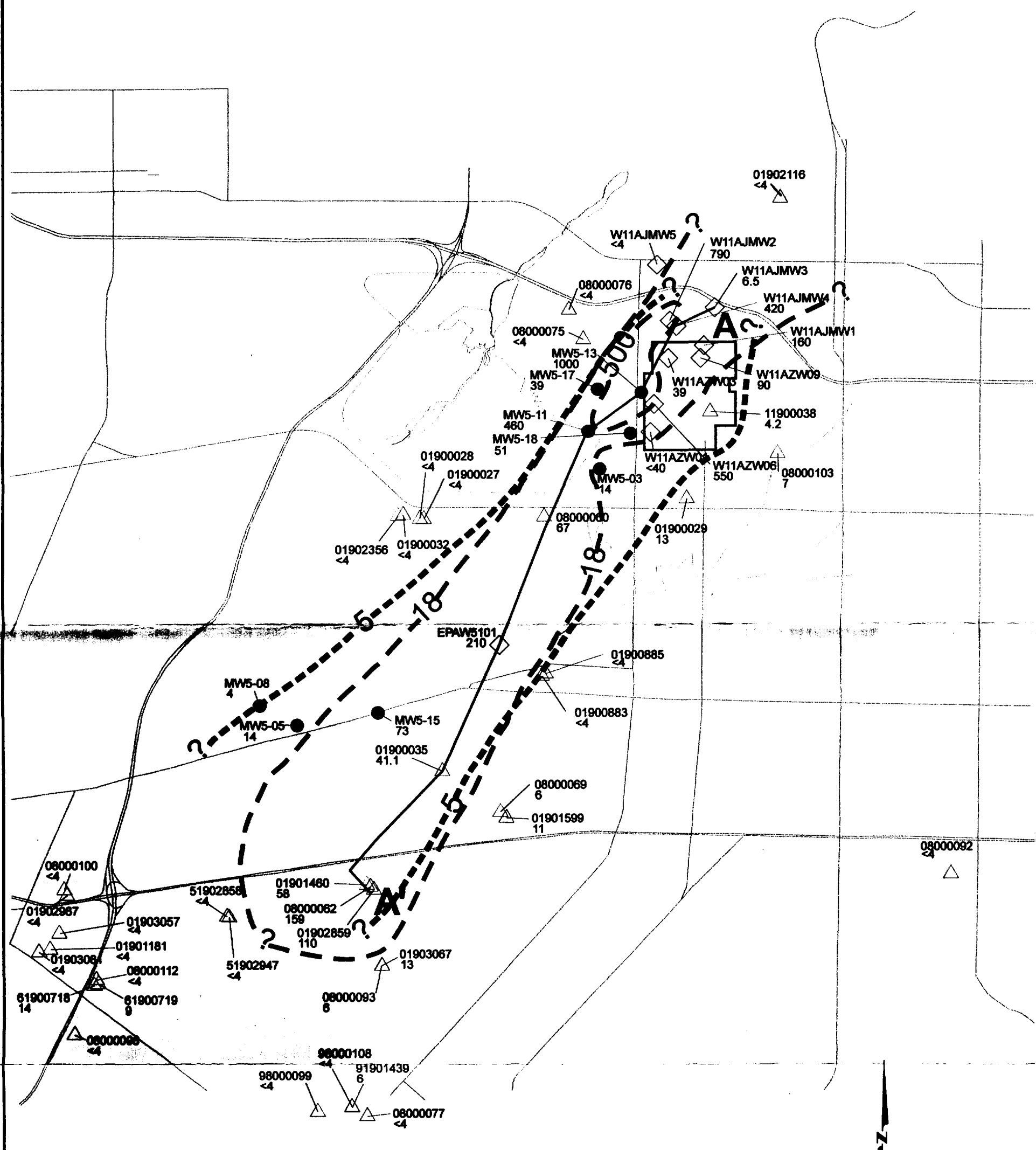
EXPLANATION

● PRE-DESIGN WELL

◇ MONITORING WELL

△ PRODUCTION WELL

ND NOT DETECTED

▬ ▬ ▬ ▬ ▬ TCE CONTOUR

▬ ▬ ▬ PERCHLORATE CONTOUR

▬▬▬▬ CROSS SECTION A-A'

NOTE: ALL UNITS IN ug/L

HLA Harding Lawson Associates
Engineering and
Environmental Services

MAXIMUM PERCHLORATE
CONCENTRATIONS IN GROUNDWATER
JUNE 1997
Baldwin Park Operable Unit
Baldwin Park, California

FIGURE

1-1

DRAWN	PROJECT-TASK NUMBER	APPROVED	DATE	REVISED DATE
SAS/JTL	37933,004		9/97	

Air scour discharge

Backwash effluent

Regenerated carbon in

Carbon column influent

Top of carbon bed

Surface wash in

Carbon slurry motive water in

Surface wash agitator

Underdrain nozzle

Plenum plate

Carbon column effluent

Plenum support plate

Spent carbon drawoff

Spent carbon out

Backwash influent

Plenum area

Air scour in

Carbon column drain

REFERENCE: WASTEWATER ENGINEERING, METCALF AND EDDY, 1991

Harding Lawson Associates
Engineering and
Environmental Services

TYPICAL GRANULAR ACTIVATED-CARBON CONTACTOR
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

FIGURE

4-1

DRAWN	PROJECT–TASK NUMBER	APPROVED	DATE	REVISED DATE
JTL	37933–003		9/97	

BIG DALTON GAC

Legend:
- 5 days
- 7 days
- 12 days
- 19 days
- 24 days

Y-axis: Perchlorate concentration (ug/L)

X-axis: INFLUENT, 1/4, 1/2, 3/4, EFFLUENT

Harding Lawson Associates
Engineering and
Environmental Services

DRAWN
JTL

PROJECT–TASK NUMBER
37933–003

APPROVED

DATE
9/97

REVISED DATE

FIGURE

**PERCHLORATE CONCENTRATION ACROSS
THE BIG DALTON GAC BED**
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

4-2

Acid Dilution and
Slow Rinse Supply

Dilute Acid
and Slow Rinse

Dilute Caustic
and Slow Rinse

Pressure
Regulating Valve

Air Relief

Raw Water

Flow
Indicator

Totalizing Meter

To Storage

Conductivity Cell

Waste

Waste Sump

REFERENCE: PERRY'S CHEMICAL ENGINEERS' HANDBOOK, ROBERT H. PERRY, DON W. GREEN, 1997

FIGURE

**TYPICAL TWO-BED
DEIONIZING SYSTEM**
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

4-3

DRAWN	PROJECT-TASK NUMBER	APPROVED	DATE	REVISED DATE
JTL	37933-003		9/97	

ELECTRODE PLAN VIEW

THREADED RODS (TYP)

CO-ALIGNED APPERTURES

CARBON AEROGEL COMPOSITE ELECTRODE

THREADED ROD

COMPRESSION RING

CARBON AEROGEL COMPOSITE

ELONGATED APERTURES (TYP)

PERIPHERAL HOLES (TYP)
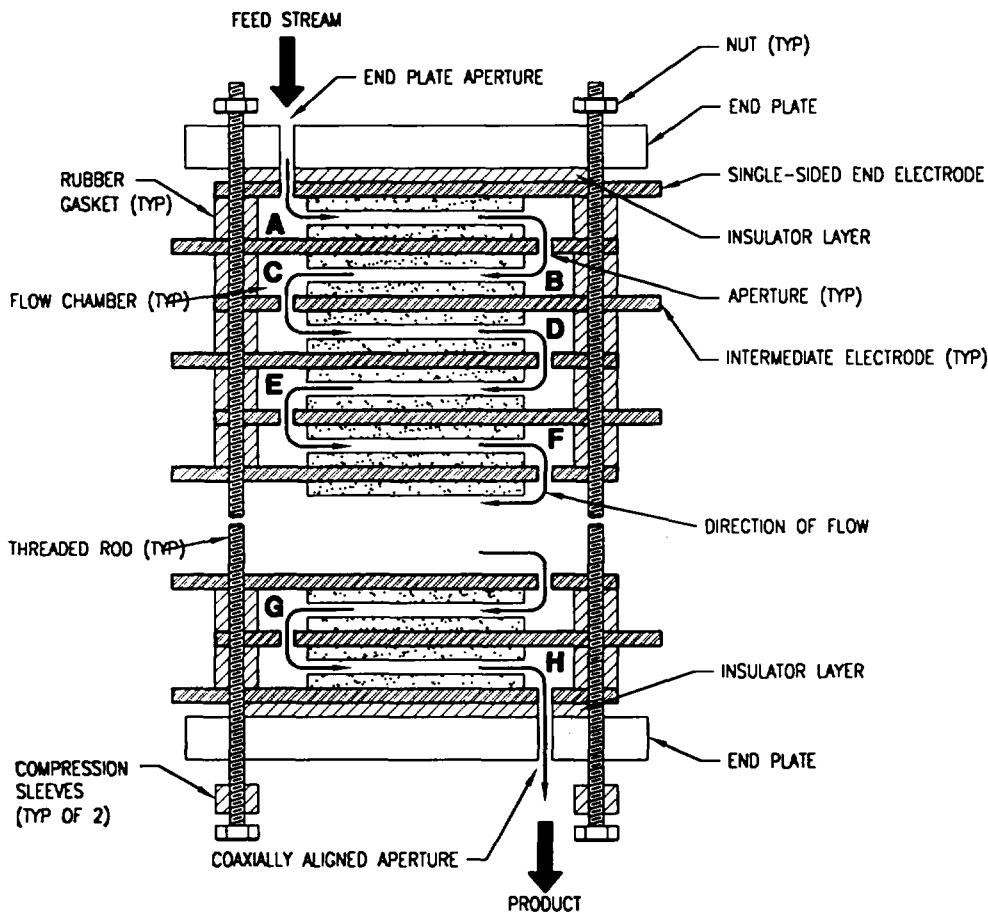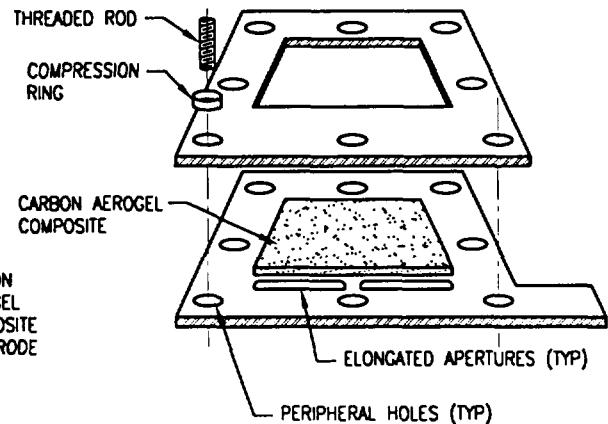
ELECTROCHEMICAL CELL SIDE VIEW

FEED STREAM

END PLATE APERTURE

NUT (TYP)

END PLATE

SINGLE-SIDED END ELECTRODE

INSULATOR LAYER

APERTURE (TYP)

INTERMEDIATE ELECTRODE (TYP)

RUBBER GASKET (TYP)

FLOW CHAMBER (TYP)

DIRECTION OF FLOW

THREADED ROD (TYP)

INSULATOR LAYER

END PLATE

COMPRESSION SLEEVES (TYP OF 2)

COAXIALLY ALIGNED APERTURE

PRODUCT

A B C D E F G H

REFERENCE: U.S. PATENT 5,425,858

FIGURE

CAPACITIVE DEIONIZATION ELECTROCHEMICAL CELL
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

4-4

MICROMETERS (LOG SCALE)	0.001	0.01	0.1	1.0	10	100	1000

MOLECULAR WEIGHT   100   200 1,000 10,000 20,000   100,000   500,000

RELATIVE SIZE OF COMMON MATERIALS

AQUEOUS SALT

CARBON BLACK

PAINT PIGMENT

GIARDIA CYST

PYROGEN

YEAST CELL

BEACH SAND

METAL ION

VIRUS

BACTERIA

PESTICIDES

POLLEN

GRANULAR ACTIVATED CARBON

SUGAR

COLLOIDAL SILICA

ASBESTOS

MILLED FLOUR

PROCESS FOR SEPARATION

REVERSE OSMOSIS

ULTRAFILTRATION

CONVENTIONAL FILTRATION

NANOFILTRATION

MICROFILTRATION

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DRAWN	PROJECT-TASK NUMBER	APPROVED	DATE	REVISED DATE
JTL	37933-003		9/97	

MEMBRANE PERFORMANCE
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

PLATE

4-5

Principle of electrodialysis. ○ Positive ion (*e.g.*, sodium) □ Negative ion (*e.g.*, chloride). *C* and *A* cation and anion permeable membrane, respectively. Ion migration under action of electric current causes salt depletion in alternate compartments and salt enrichment in adjacent ones. (*Spiegler, "Salt Water Purification," Wiley, New York, 1962.*)

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Environmental Services

DRAWN	PROJECT—TASK NUMBER	APPROVED	DATE	REVISED DATE
JTL	37933—003		9/97	

FIGURE

PRINCIPLE OF ELECTRODIALYSIS
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

4-6

SHIELDING

HEAT
EXCHANGERS

PRESSURE LET-DOWN
VALVE

CHECK
VALVES

HEATERS

OXIDIZER
PUMP

FUEL
PUMP

PROGRAMMABLE
TEMPERATURE
CONTROLLER

FTIR/WHITE CELL

VACUUM
MANIFOLD

LEAK VALVE

GAS-LIQUID
SEPARATOR

MASS
SPECTROMETER

PUMPS

PUMPS

**SCHEMATIC OF LINEAR FLOW REACTOR
FOR SUPER CRITICAL WATER OXIDATION**
Baldwin Park Operable Unit Steering Committee
Baldwin Park, California

PLATE

4-7

WATER AND OXYGEN ←————————————————→ PURIFIED STREAM WITH REDUCED
AMOUNT OF OXYCHLORINE SPECIES,
CHLORIDE, AND HYDROGEN

CATION MEMBRANE

HIGH SURFACE AREA CATHODE

TEFLON MESH SPACER

CATHODE CURRENT DISTRIBUTOR

+

-

ANODE

ANOLYTE COMPARTMENT

CATHOLYTE COMPARTMENT

DEIONIZED WATER

AQUEOUS SOLUTION CONTAINING
OXYCHLORINE SPECIES

REFERENCE: U.S. PATENT 5,167,777

ADMINISTRATION BUILDING LAYOUT

Perchlorate Treatment Technology Screening
Baldwin Park, California

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
TEM	37933,004		9/97	

TREATMENT BUILDING LAYOUT

Labels within figure:
- MONORAIL
- 60'
- 9"(TYP)
- 6"(TYP)
- 15'
- 15'
- BI-FOLD DOOR
- CHLORINE SCRUBBER ROOM
- RAMP DOWN
- SCRUBBER MANIFOLD
- CHLORINE GAS DETECTOR
- CAUSTIC STORAGE/ CHLORINE SCRUBBER
- PUMP
- FAN
- CHLORINE STORAGE ROOM
- DETECTOR
- CHLORINE FEEDER ROOM
- CHLORINE FEEDER
- CHLORINE 1-TON CYLINDER (TYP)
- FLOOR VENT
- CHLORINE BOOSTER PUMP
- 13'
- 9.5'
- 40'
- SPARE PARTS/MAINTENANCE EQUIP. ROOM
- 15'
- 25'
- VARIES
- PERCHLORATE TREATMENT AREA (SIZE VARIES DEPENDING ON TREATMENT METHOD)
- OVERHEAD DOOR (TYP)
- 0   5   10
- Scale in feet

Harding   Lawson   Associates
Engineering and
Environmental Services

TREATMENT BUILDING LAYOUT

Perchlorate Treatment Technology Screening
Baldwin Park, California

FIGURE

6-2

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
TEM	37933,004		9/97	

BIOLOGICAL GAC/FB
REACTOR
(TYP OF 12)

HIGH-RATE
MULTI-MEDIA FILTER
(TYP OF 8)

POLYMER

BACKWASH WATER

NUTRIENTS

METHANOL

INFLUENT
GROUNDWATER

CHLORINE

TO POTABLE
WATER SYSTEM

DISTRIBUTION
PUMP
(TYP OF 5)

TREATED WATER
RESERVOIR

COMPRESSOR

BACKWASH
PUMP

RECLAIMED BACKWASH WATER

ALUM

BACKWASH WATER
STORAGE TANK

FLOCCULATION/
CLARIFICATION BASIN

RECLAMATION
SYSTEM PUMP

BACKWASH WATER
LAGOON

SLUDGE
DISPOSAL

FILTER
PRESS

BACKWASH WATER

GAC FINES
AND SETTLING
STORAGE BASIN

CARTRIDGE
FILTER
(TYP OF 6)

GAC
CONTACTOR
(TYP OF 11)

GAC FINES

SPENT FINES
FOR DISPOSAL

TO POTABLE
WATER SYSTEM

INFLUENT
GROUNDWATER

SPENT GAC

BACKWASH WATER

REGENERATED GAC

CARBON
REGENERATION

	GAC SYSTEM PROCESS SCHEMATIC	FIGURE
Harding Lawson Associates Engineering and Environmental Services	Perchlorate Treatment Technology Screening Baldwin Park, California	6-4

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
JTL	37933,004		9/97	

ION EXCHANGE
PRESSURE VESSEL
(TYP OF 28)

REGENERATE

REGENERATE
STORAGE

REGENERATE
PUMP

CARTRIDGE
FILTER
(TYP OF 6)

CHLORINE

TO POTABLE
WATER SYSTEM

INFLUENT
GROUNDWATER

REGENERATION
RINSE WATER

TREATED BRINE

RECLAIMED BACKWASH WATER

BRINE TREATMENT SYSTEM
(SEE SEPARATE DRAWING)

TO BACKWASH WATER STORAGE TANK

Harding Lawson Associates Engineering and Environmental Services	ION EXCHANGE SYSTEM PROCESS SCHEMATIC Perchlorate Treatment Technology Screening Baldwin Park, California	FIGURE **6-5**
DRAWN TEM	**JOB NUMBER** 37933,004	**APPROVED**	**DATE** 9/97	**REVISED DATE**
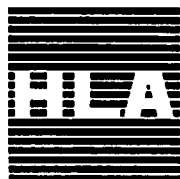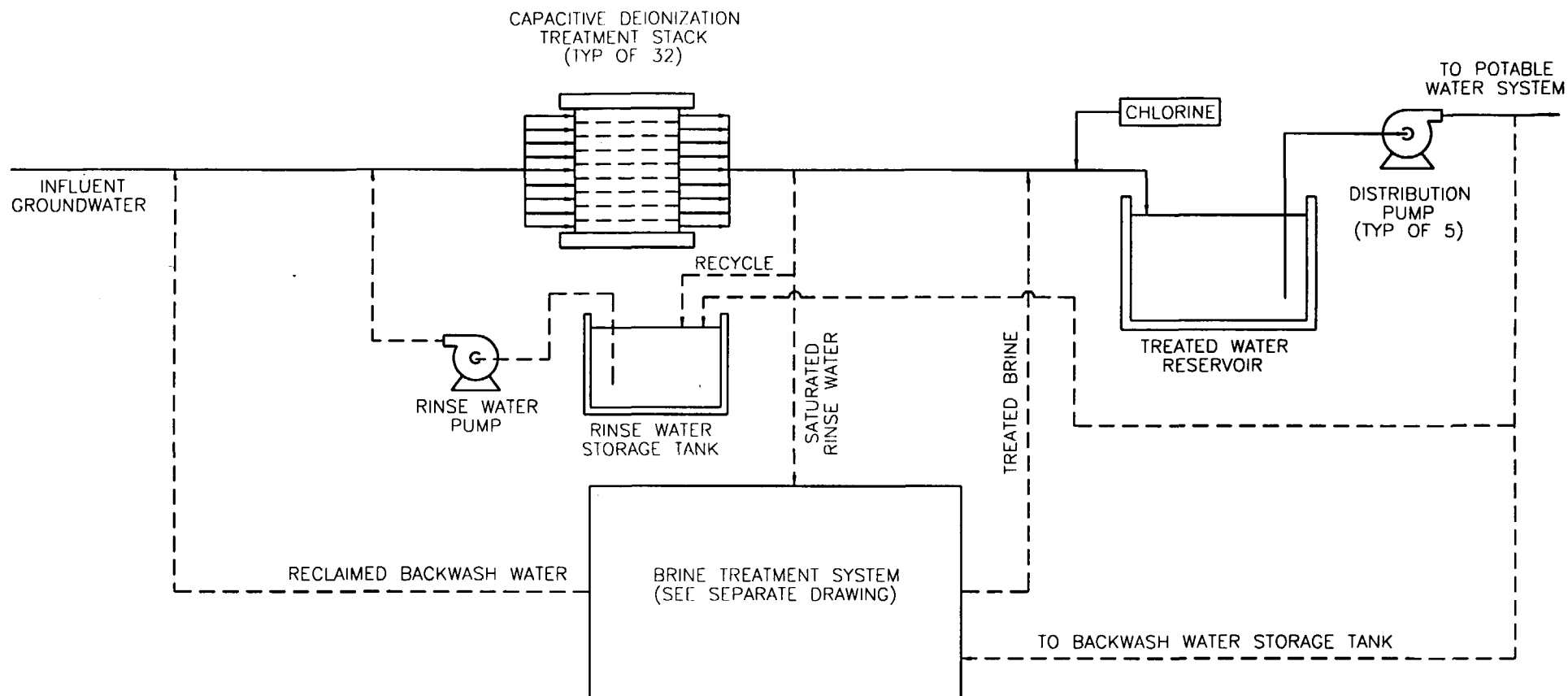
CAPACITIVE DEIONIZATION
TREATMENT STACK
(TYP OF 32)

TO POTABLE
WATER SYSTEM

CHLORINE

INFLUENT
GROUNDWATER

RECYCLE

DISTRIBUTION
PUMP
(TYP OF 5)

RINSE WATER
PUMP

RINSE WATER
STORAGE TANK

SATURATED
RINSE WATER

TREATED BRINE

TREATED WATER
RESERVOIR

RECLAIMED BACKWASH WATER

BRINE TREATMENT SYSTEM
(SEE SEPARATE DRAWING)

TO BACKWASH WATER STORAGE TANK

Harding Lawson Associates
Engineering and
Environmental Services

DRAWN	JOB NUMBER	APPROVED	DATE
TEM	37933,004		9/97

**CAPACITIVE DEIONIZATION SYSTEM
PROCESS SCHEMATIC**

Perchlorate Treatment Technology Screening
Baldwin Park, California

FIGURE

6-6

REVISED DATE

CARTRIDGE
FILTER
(TYP OF 6)

ANTISCALANT

ACID

REVERSE OSMOSIS
TREATMENT TRAIN
(TYP OF 11)

DEGASIFIER
(TYP OF 2)

PERMEATE

CAUSTIC

CHLORINE

TO POTABLE
WATER SYSTEM

INFLUENT
GROUNDWATER

HIGH PRESSURE
FEED PUMP
(TYP OF 6)

CONCENTRATE

TREATED BRINE

DISTRIBUTION
PUMP
(TYP OF 5)

TREATED WATER
RESERVOIR

RECLAIMED BACKWASH WATER

BRINE TREATMENT SYSTEM
(SEE SEPARATE DRAWING)

TO BACKWASH WATER STORAGE TANK

Harding Lawson Associates	REVERSE OSMOSIS SYSTEM PROCESS SCHEMATIC	FIGURE
Engineering and Environmental Services	Perchlorate Treatment Technology Screening Baldwin Park, California	6-7

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
TEM	37933,004		9/97	

HLA

INFLUENT GROUNDWATER

CARTRIDGE FILTER (TYP OF 6)

ELECTRODIALYSIS TREATMENT STACK (TYP OF 26)

RECLAIMED BACKWASH WATER

BRINE TREATMENT SYSTEM (SEE SEPARATE DRAWING)

CONCENTRATE

TREATED BRINE

TO BACKWASH WATER STORAGE TANK

CHLORINE

TREATED WATER RESERVOIR

DISTRIBUTION PUMP (TYP OF 5)

TO POTABLE WATER SYSTEM
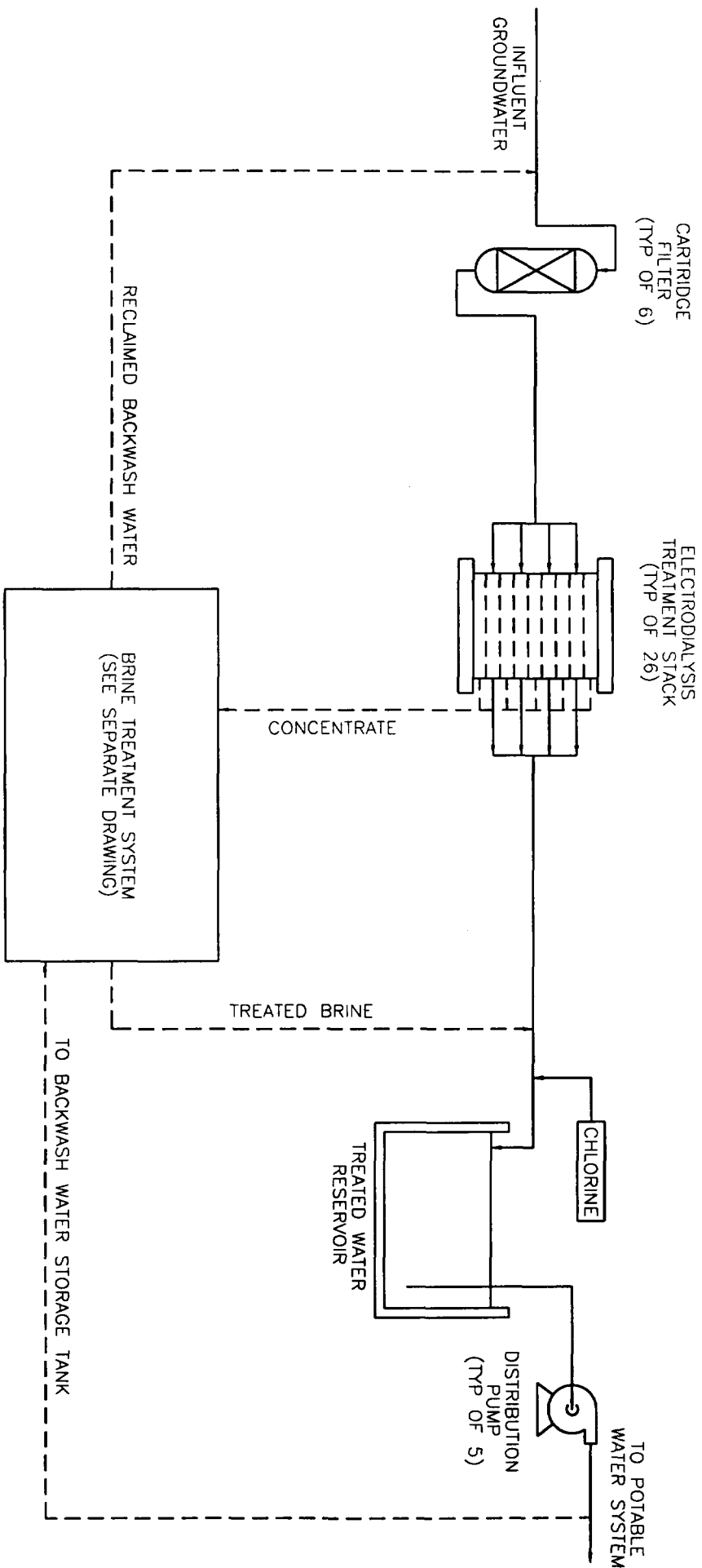
Harding Lawson Associates
Engineering and
Environmental Services

**ELECTRODIALYSIS SYSTEM
PROCESS SCHEMATIC**

Perchlorate Treatment Technology Screening
Baldwin Park, California

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
TEM	37933.004		9/97	

FIGURE **6-8**

BIOLOGICAL GAC/FB
REACTOR
(TYP OF 2)

HIGH-RATE
MULTI-MEDIA FILTER
(TYP OF 2)

POLYMER

BACKWASH WATER

NUTRIENTS

METHANOL

BRINE

BRINE
PUMP

BRINE EQUALIZATION
TANK

TREATED BRINE

TO TREATED
WATER RESERVOIR

FROM TREATED
WATER RESERVOIR

BACKWASH
PUMP

COMPRESSOR

ALUM

RECLAIMED BACKWASH WATER

TO TREATMENT
SYSTEM INFLUENT

BACKWASH WATER
STORAGE TANK

FLOCCULATION/
CLARIFICATION BASIN

RECLAMATION
SYSTEM PUMP

BACKWASH WATER
LAGOON

SLUDGE
DISPOSAL

FILTER
PRESS

Harding Lawson Associates

Engineering and
Environmental Services

**BRINE TREATMENT SYSTEM
PROCESS SCHEMATIC**

Perchlorate Treatment Technology Screening
Baldwin Park, California

FIGURE

6-9

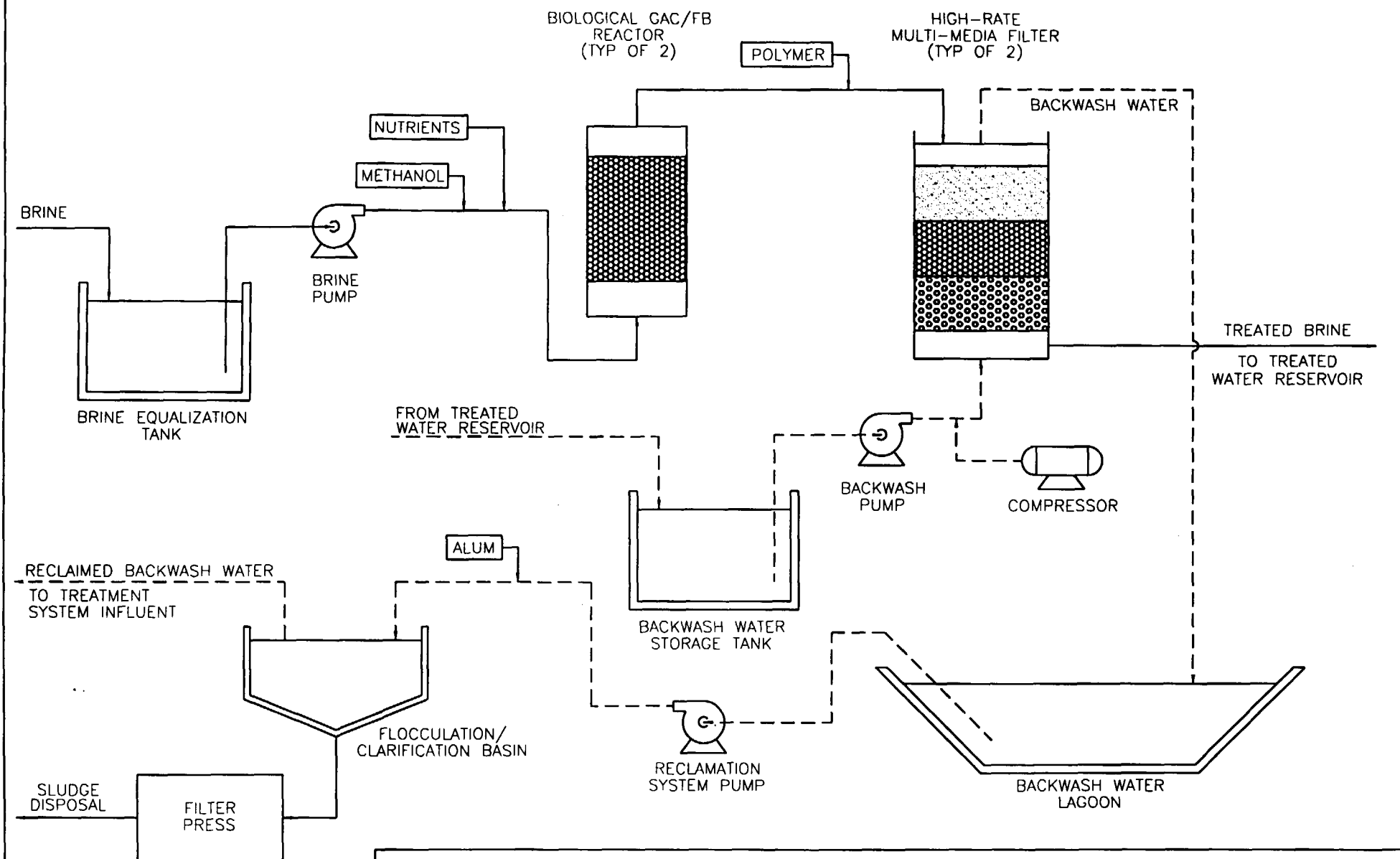| DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
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APPENDIX A

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APPENDIX A

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APPENDIX B

DIALOG DATABASES SEARCHED

APPENDIX B

DIALOG DATABASES SEARCHED

The following databases are included in the ALL SCIENCE index of Dialog and were included in all online Dialog searches.

1	INSPEC	1969-1997
2	BIOSIS Previews	1969-1997
3	National Technical Information Service (NTIS)	1997
4	Ei Compendex	1970-1997
5	Business & Industry	1994-1997
6	*IAC* Industry Express	1995-1997
7	Mechanical Engineering Abstracts	1973-1997
8	ABI/INFORM	1971-1997
9	*IAC* PROMT	1972-1997
10	*IAC* F&S Index	1980-1997
11	Employee Benefits Infosource	1986-1997
12	Meteorological & Geoastrophysical Abstracts	1970-1997
13	World Surface Coatings Abstracts	1976-1997
14	METADEX: Metals Science	1966-1997
15	Aluminum Industry Abstracts	1968-1997
16	Dissertation Abstracts Online	1860-1997
17	Pharmaceutical News Index (PNI)	1861-1997
18	Health News Daily	1990-1997
19	CAB Abstracts	1972-1997
20	Food Science and Technology Abstracts	1969-1997
21	TSCA Chemical Substances Inventory	1997
22	FOODLINE: Food Science and Technology	1972-1997
23	FOODLINE: International Food Market Data	1979-1997
24	GeoArchive	1974-1997
25	FOODLINE: Current Food Legislation	1983-1997
26	SPIN	1975-1997
27	Transportation Research Information Services (TRIS)	1970-1997
28	Global Mobility Database	1965-1997
29	Inside Conferences	1993-1997
30	World Textiles	1970-1997
31	EMBASE	1974-1997
32	International Pharmaceutical Abstracts	1970-1997
33	Life Sciences Collection	1982-1997
34	Conference Papers Index	1973-1997
35	DIALOG Source One: Engineering	1991-1997
36	TULSA (Petroleum Abstracts)	1965-1997
37	GeoRef	1785-1997
38	IHS International Standards and Specifications	1997
39	JICST-EPlus – Japanese Science & Technology	1985-1997
40	FLUIDEX (Fluid Engineering Abstracts)	1973-1997
41	Wilson General Science Full-Text	1984-1997
42	Wilson Applied Science & Technology Abstracts	1983-1997
43	ASI	1973-1997
44	Energy Science and Technology	
45	Aerospace Database	1962-1997
46	Nuclear Science Abstracts	1948-1976
47	*IAC* National Newspaper Index	1979-1997

48	Textile Technology Digest	1978-1997
49	CLAIMS/Reassignment & Reexamination	1997
50	CLAIMS/U.S. Patents Abstracts Weekly	1997
51	Federal Register Abstracts	1977-1993
52	PASCAL	1973-1997
53	IAC Trade & Industry Database	1976-1997
54	IAC Legal Resource Index	1980-1997
55	MEDLINE	1966-1997
56	TOXLINE	1965-1997
57	DIOGENES FCA Regulatory Updates	1976-1997
58	Occupational Safety and Health (NIOSHTIC)	1973-1997
59	Insurance Periodicals Index	1984-1997
60	EMBASE Alert	1997
61	F-D-C Reports	1987-1997
62	NDA Pipeline: New Drugs	1991-1997
63	Industry Trends and Analysis	1997
64	Health Devices Alerts	1977-1997
65	Information Science Abstracts	1966-1997
66	IAC Newsearch	1997-1997
67	Microcomputer Abstracts	1974-1997
68	Buyer's Guide to Micro Software (SOFT)	1993
69	Abstracts in New Technologies and Engineering (ANTE)	1981-1997
70	MathSci	1940-1997
71	PAPERCHEM	1967-1997
72	Electric Power Database	1972-1997
73	PIRA (Packaging, Paper, Printing and Publishing, Imaging, and Nonwovens Abstracts	1975-1997
74	Packaging Science and Technology Abstracts	1982-1997
75	SoftBase: Reviews, Companies, and Products	1997
76	API EnCompass: News	1975-1997
77	Federal Research in Progress (FEDRIP)	1997
78	Materials Business File	1985-1997
79	IAC Computer Database	1983-1997
80	MicroComputer Software Guide OnLine	1997
81	GEOBASE	1980-1997
82	Engineered Materials Abstracts	1986-1997
83	World Translations Index	1979-1997
84	Kirk-Othmer Encyclopedia of Chemical Technology	1995
85	Analytical Abstracts	1980-1997
86	Dictionary of Substances and Their Effects (DOSE)	1997
87	Chemical Engineering and Biotechnology Abstracts	1970-1997
88	Chemical Safety NewsBase	1981-1997
89	Chemical Business NewsBase	1984-1997
90	PLASPEC Materials Selection Database	1997
91	Polymer Online	
92	RAPRA: Rubber and Plastics	1972-1997
93	Material Safety Data Sheets – OHS	1997
94	Material Safety Summary Sheets – OHS	1997
95	Material Safety Label Data – OHS	1997
96	Ceramic Abstracts	1976-1996
97	Registry of Toxic Effects of Chemical Substances (RTECS)	1997
98	CHEMTOX Online	19970
99	CLAIMS/U.S. Patents Abstracts	1950-1997
100	Chinese Patent Abstracts in English	1985-1997
101	INPADOC/Family and Legal Status	1997

102	JAPIO	1976-1997)
103	European Patents Fulltext	1978-1997
104	Derwent World Patents Index (WPI)	1963-1997
105	APIPAT	1964-1997
106	APILIT	1965-1997
107	Derwent Drug File	1964-1982
108	Derwent Drug File	1983-1997
109	PEDS: Defense Program Summaries	1997
110	Adis Newsletters (Current)	1997
111	Adis Newsletters (Archive)	1982-1997
112	SciSearch: Cited Reference Science Database	1974-1997
113	American Medical Association Journals	1982-1997
114	New England Journal of Medicine	1985-1997
115	IMSworld Patents International	1997
116	The Lancet	1986-1997
117	Delphes European Business	1980-1997
118	Accounting and Tax Database	1971-1997
119	ESPICOM Telecommunication/Power Reports	1997
120	KR Investment Research Index	1995-1997
121	Investext	1982-1997
122	ICC International Business Research	1986-1997
123	Jane's Defense and Aerospace News/Analysis	1997
124	DMS/FI Market Intelligence Reports	1997
125	Knight-Ridder/Tribune Business News	1992-1997
126	*IAC* New Product Announcements/*Plus*	1985-1997
127	McGraw-Hill Companies Publications Online	1985-1997
128	Business Dateline	1985-1997
129	*IAC* Newsletter Database	1987-1997
130	Journal of Commerce	1986-1997
131	CMP Computer Fulltext	1988-1997
132	*IAC* Newswire ASAP	1997
133	U.S. Patents Fulltext	1971-1979
134	U.S. Patents Fulltext	1980-1989
135	U.S. Patents Fulltext	1990-1997
136	BNA Daily News from Washington	1990-1997
137	Federal News Service	1991-1997
138	Federal Acquisition Regulations (FARS)	1990-1991
139	Federal Register	1988-1997
140	Computer News Fulltext	1989-1997
141	KR Telecommunications Newsletters	1995-1997
142	Freedonia Market Research	1990-1997
143	BCC Market Research	1989-1997
144	Frost & Sullivan Market Intelligence	1992-1997
145	Jupiter Market Research	1997
146	Textline Global News	1980-1989
147	Textline Global News	1990-1994
148	Tax Notes Today	1986-1997
149	State Tax Daily	1991-1997
150	Worldwide Tax Daily	1987-1997
151	Court Petitions and Complaints	1994-1997
152	Textline Current Global News	1995-1997

APPENDIX C

KEY WORDS USED DURING DATABASE SEARCH

APPENDIX C

KEY WORDS USED DURING DATABASE SEARCH

1. Granulated activated carbon fluidized bed
2. Biological reduction
3. Chemical reduction
4. Ammonium perchlorate or perchlorate
5. Chlorate or Chlorate dioxide
6. Nitrate or Denitrification
7. Groundwater or Aqueous
8. Reverse osmosis
9. Ion exchange
10. Anaerobic reactor
11. Clean or Treat or Remediate
12. Propellant
13. Wastewater treatment or Purification
14. Oxidation
15. Electrodialysis reversal
16. Electrochemical reduction
17. Catalyzed chemical reduction
18. Copper catalyzed reduction
19. Catalyst
20. Zeolite or Bimetallic or ((Nickel or Copper) and Iron)

APPENDIX D

PATENTS

Process and Apparatus for the Removal of Oxyhalide Species
from Aqueous Solutions
Patent Number: 5,167,777
Date of Patent: December 1, 1992
Assignee: Olin Corporation, Cheshire, Connecticut

US005167777A

[54] PROCESS AND APPARATUS FOR THE REMOVAL OF OXYHALIDE SPECIES FROM AQUEOUS SOLUTIONS

[75] Inventors: Jerry J. Kaczur; David W. Cawlfield; Kenneth E. Woodard, all of Cleveland, Tenn.

[73] Assignee: Olin Corporation, Cheshire, Conn.

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3,823,225	7/1974	Sprague	423/478
4,444,631	4/1984	Bommaraju et al.	204/128
4,456,510	6/1984	Murakami et al.	204/101
4,465,533	8/1984	Covitch	204/282
4,627,899	12/1986	Smith et al.	204/112
4,731,169	3/1988	Lipsztajn	204/130

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Article entitled "Kinetics of the Reduction of Chlorite Ion" by She-Huang Wu and Jiann-Kuo-Wu in the TATUNG Journal, vol. XVI, pp. 253-256, Nov. 1986.

[57] ABSTRACT

A process for electrochemically treating an aqueous solution containing inorganic oxyhalide species is disclosed in which the aqueous solution is fed into the catholyte compartment of an electrochemical reduction cell using a high surface area cathode separated from an anolyte compartment to electrochemically reduce substantially all of the oxyhalide species to halide ions and produce a purified water product.
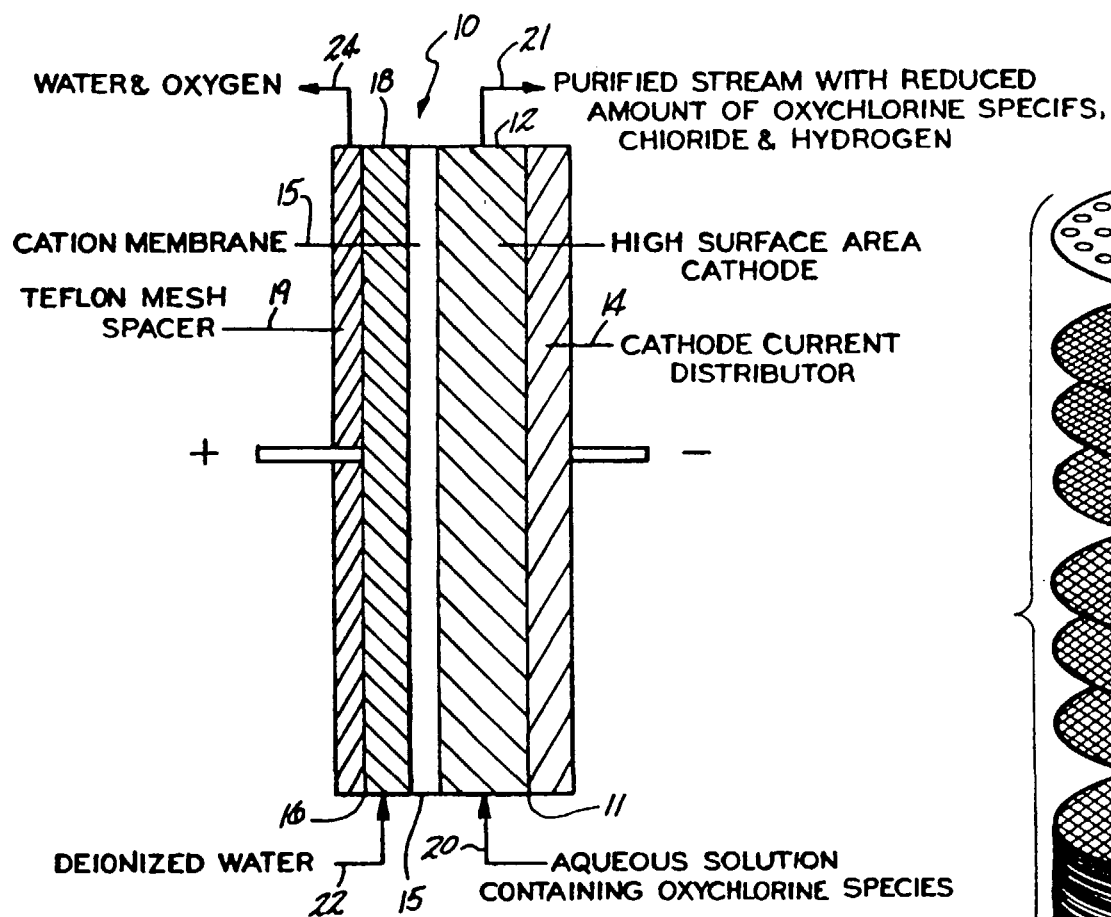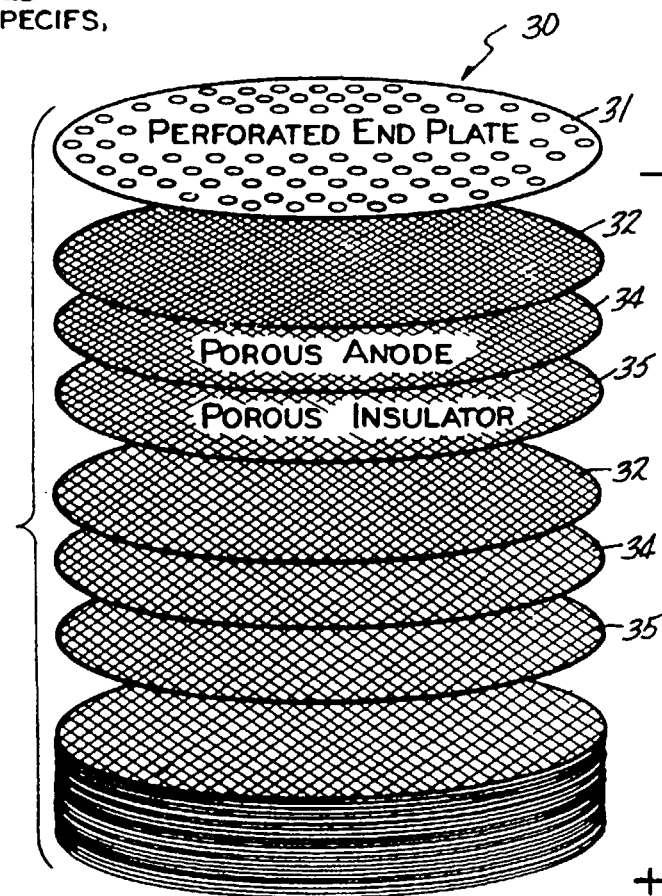
30 Claims, 1 Drawing Sheet
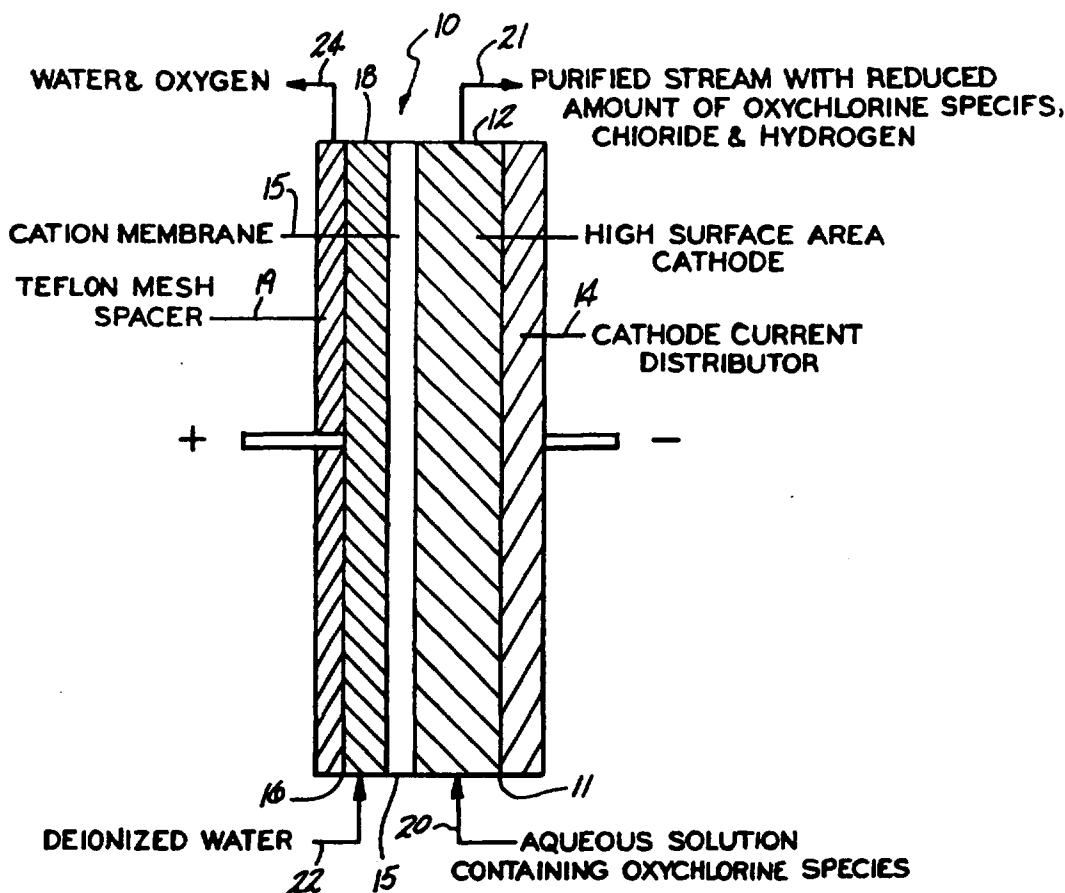
WATER & OXYGEN

24 *10* *21*

18

12

PURIFIED STREAM WITH REDUCED
AMOUNT OF OXYCHLORINE SPECIFS,
CHIORIDE & HYDROGEN

CATION MEMBRANE

15

HIGH SURFACE AREA
CATHODE

TEFLON MESH
SPACER

19

14

CATHODE CURRENT
DISTRIBUTOR

+

—

16

11

DEIONIZED WATER

20

AQUEOUS SOLUTION
CONTAINING OXYCHLORINE SPECIES

22 *15*

FIG-1

PERFORATED END PLATE

30

31

32

34

POROUS ANODE

35

POROUS INSULATOR

32

34

35

+

FIG-2

1

PROCESS AND APPARATUS FOR THE REMOVAL OF OXYHALIDE SPECIES FROM AQUEOUS SOLUTIONS

BACKGROUND OF THE INVENTION

This invention relates generally to the production of purified aqueous solutions. More particularly, the present invention relates to the electrochemical reduction of oxychlorine species in aqueous solutions to remove such species by reducing them to environmentally safe chloride ions. The process and the apparatus employing the process are suitable for both waste water and potable water treatment. The electrochemical reduction occurs on a high surface area cathode structure. Both dilute and concentrated solutions of oxychlorine species can be reduced to environmentally safe chlorides by the process and apparatus of this invention.

Chlorine dioxide is widely used as an oxidizer and disinfectant for taste and odor control in drinking water and as a bleaching agent in the production of pulp and paper. It is also used for the oxidation of trihalomethane precursors in drinking water. Most of the chlorine dioxide generators used in drinking water treatment employ a 95-98% efficient chemical reaction between chlorine gas and sodium chlorite. The unreacted sodium chlorite remains as an oxyhalide that is increasingly undesirable both toxicologically and environmentally in drinking water.

In the commercial environment of pulp and paper mills, large volumes of chlorine dioxide are generated from the combined reaction of a chlorate salt, acid, and a reducing agent. Alkali metal or alkaline earth chlorate salts are employed with the typical being sodium chlorate. Common acids used in the process are sulfuric or hydrochloric. Representative reducing agents used are sodium chloride, methanol or sulfur dioxide. These reagents are used in various combinations depending upon the specific chlorine dioxide process employed. The aqueous flow streams from these processes all have the potential to contain significant amounts of unreacted chlorate, as well as chlorite and chlorate by-products produced from pulp and paper bleaching processes.

In drinking water applications, the by-products of chlorine dioxide treatment pose a major problem. These by-products are chlorite and chlorate. Chlorite is the principal by-product produced from the reaction of trihalomethane precursors and chlorine dioxide. Chlorate, once formed either from the chlorine dioxide generator or from by-product reactions, is not easily removed chemically. Previous approaches attempted to remove chlorite from drinking water by using sulfur-based reducing agents, such as sulfur dioxide, sodium bisulfite, and sodium sulfite. Unfortunately, these reducing agents produce chlorate as a major by-product of complex side reactions with oxygen in water. Another approach has used sodium thiosulfate as a reducing agent which does not produce significant amounts of by-product chlorate. Thiosulfate, however, suffers from safety considerations because of unwanted sulfur-oxygen by-products produced in the water.

These and other problems are solved in the process and by the apparatus employing the process of the present invention by removing both chlorite and chlorate from aqueous solutions, as well as other oxychlorine

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species, from aqueous solutions by the use an electrochemical reduction process.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process to remove oxychlorine species, including chlorites and chlorates, from aqueous solutions as a part of a major water treatment process for waste water and potable water.

It is another object of the present invention to provide a process and apparatus for employing the process to treat dilute aqueous solutions by electrochemically reducing oxychlorine species therein and to remove them from the solution by reducing the oxychlorine species to environmentally safe chloride ions.

It is a feature of the present invention that the electrochemical reduction process can remove trace transition metal ions from the aqueous solution by depositing them onto the cathode surface.

It is another feature of the present invention that the electrochemical reduction process can be combined as a part of the method of treating drinking water in combination with the chlorine dioxide oxidizing and disinfecting treatment system.

It is another feature of the present invention that a high surface area cathode is employed in the process and the apparatus employing the process of the present invention.

It is yet another feature of the present invention that the electrochemical reduction process operates at a high efficiency wherein the sum of the current efficiency and the removal efficiency of the oxychlorine species is greater than about 50%.

It is an advantage of the present invention that the electrochemical reduction process can be used in an electrochemical cell to convert both low or high concentrations of oxychlorine species in aqueous solutions to environmentally safe chloride ions.

It is another advantage of the present invention that chlorine dioxide may be used in combination with the instant process as an oxidizer for the destruction of trihalomethane precursors in drinking water treatment.

It is still another advantage of the present invention that the electrochemical reduction process allows the use of more efficient levels of oxidizing disinfectants, such as chlorine dioxide and chlorine, without leaving traces of their by-products in potable water treatment.

It is yet another advantage of the present invention that waste water effluents containing high levels of oxychlorine species, such as chlorate from bleaching applications, can be substantially reduced to environmentally safe chloride ions.

These and other objects, features and advantages are obtained in the process and the apparatus employing the process of the present invention by feeding an aqueous solution to be electrochemically reduced in a catholyte compartment of an electrochemical cell having a separator between the catholyte compartment and the anolyte compartment and using a high surface area cathode to electrochemically reduce substantially all of the oxyhalide species in the aqueous solution to halide ions.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, features and advantages of the invention will become apparent upon consideration of the following detailed disclosure of the invention especially when is taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a side elevational view of an electrochemical reduction cell; and

FIG. 2 is an exploded view of a bipolar flow-through electrochemical cell stack.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 shows an electrochemical cell that can be employed to reduce the concentration of oxychlorine species in aqueous solutions to environmentally safe chloride ions. The cell is indicated generally by the numeral 10. Cell 10 comprises a catholyte compartment 11 and a anolyte compartment 16 separated by a separator 15. The separator 15 can be a diaphragm if the anode reaction doesn't generate chlorine or other undesirable products. It must be kept separate from the catholyte products. Alternately, and more preferably, the separator 15 is a permselective cation exchange membrane. Suitable cation exchange membranes are those sold under the NAFION ® trademark by E. I. DuPont de Nemours and Company, the membranes sold under the FLEMION ® trademark produced by Asahi-Glass Company. Hydrocarbon based membranes can also be used depending on their suitability at the cell's operating parameters, such as temperature.

The catholyte compartment 11 contains a high surface area cathode 12 that has a specific surface area of greater than about 50 cm^2/cm^3 and is made from a high hydrogen overvoltage material. A cathode current distributor 14 is provided to distribute current to the cathode. The cathode current distributor 14 preferably is a solid distributor backplate but may also be perforated. The high surface area cathode 12, the current distributor plate 14 and the separator or cation exchange membrane 15 are mounted or assembled in direct contact in a zero-gap spacing arrangement.

The anolyte compartment 16 contains an anode material 18 that may be of expanded titanium metal with an oxygen catalyst coating. A spacer 19 is provided, functioning as a gas disengagement device, as well as providing physical spacing of the anode 18 from the separator 15 when the separator is an ion exchange membrane. A catholyte feed line 20 is diagrammatically illustrated as feeding aqueous solution into the bottom of the cell 10, while a catholyte compartment outlet line 21 is shown to remove the product of the reduction of the oxychlorine species. Where anolyte is used, an anolyte feed line 22 is provided to feed either deionized water, softened water or non-oxidizing acids to the anolyte compartment 16. The cell 10 can be operated in an anolyteless configuration when using a microporous diaphragm or in low current density operation with a water permeable separator.

Where an anolyte solution is provided, the solution flows through the anolyte compartment 16 to supply water for the oxidation of water at the electrode surface according to an oxidation reaction of:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
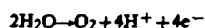
Oxygen gas is externally disengaged in an anolyte gas disengager (not shown). The aqueous solution being reduced is fed in through the catholyte feed line 20 to the high surface area cathode 12 where the oxychlorine species are electrochemically reduced on the cathode surface through various lower chlorine valence reduced chlorine-oxygen intermediates, finally ending as chloride ions. The reduced solution and any by-product halogen produced then exits the cell through the catho-

lyte compartment outlet line 21 to flow to an external catholyte disengager (not shown) to separate hydrogen gas from the water stream. Hydrogen gas can be produced by the competing water reduction reaction that can occur at the cathode surface and reduce the efficiency of the reduction as follows:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-.$$
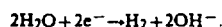
The electrochemical reduction efficiency of the high surface area cathode is dependent upon a number of variables, such as the concentration of the oxychlorine species, the flow rate of the aqueous solution through the high surface area cathode structure, the number of electrons required for the reduction of each oxychlorine species, the residence time of the solution in the cathode, the high surface area cathode density, the cathode specific surface area, the hydrogen overvoltage and the electrochemical characteristics of the cathode material employed. One advantage of the present invention is that the electrochemical reduction is done at high efficiency since the sum of the current efficiency and the removal efficiency of the oxychlorine species is greater than about 50%. The current efficiency is defined as the Faraday equivalent of the electrochemical reduction of the oxychlorine species reduced to chloride ions divided by the number of Faradays of electricity used.

The oxychlorine species that can be reduced can include chlorine dioxide, chlorate, perchlorate, hypochlorous acid, hypochlorite, chlorine and chlorites. The net reduction reactions and the standard potentials for these reactions for these oxychlorine species in acid solutions are as follows:

$ClO_2^- + 4H^+ + 4e^-$ $E_o = -1.599$ Volts	$\rightarrow$	$Cl^- + 2H_2O$
$ClO_3^- + 6H^+ + 6e^-$ $E_o = -1.451$ Volts	$\rightarrow$	$Cl^- + 3H_2O$
$ClO^{4-} + 8H^+ + 8e^-$ $E_o = -1.389$ Volts	$\rightarrow$	$Cl^- + 4H_2O$
$HClO + H^+ + 2e^-$ $E_o = -1.494$ Volts	$\rightarrow$	$Cl^- + H_2O$
$ClO^- + 2H^+ + 2e^-$ $E_o = -1.715$ Volts	$\rightarrow$	$Cl^- + 2H_2O$
$ClO_2 + 4H^+ + 5e^-$ $E_o = -1.511$ Volts	$\rightarrow$	$Cl^- + 2H_2O$

Although only chloride and oxychlorine species reduction are described in the above equations, it is to be understood that this is equally well effective for any oxyhalide species reduction. The oxyhalide species can be a halide selected from the group consisting of bromine, fluorine and iodine, as well as chlorine.

An additional benefit from the use of the present electrochemical reduction process is that trace transition metal ions may be removed from the aqueous solution by being deposited onto the cathode surface. Typical metals that can be so removed include iron, nickel, zinc. These deposited metallic ions can be removed periodically by acid treatment of the cathode in situ or by replacing the cathode after a predetermined number of hours of operation. The periodic acid treatment of the cathode can help remove any alkaline earth deposits that may precipitate or form on the surface, such as calcium hydroxide or magnesium hydroxide.

The aqueous solution fed into the cell through catholyte feed line 20 may be either acidic or alkaline and the pH may be adjusted to optimize the desired reduction.

The normal operating pH range can be from about 2 to about 13, but more preferably is from about 3 to about 11. For maximum reduction of chlorate ions in the aqueous solution, a feed pH of less than about 7 and preferably less than about 3 is desirable. However, chlorite reduction can be accomplished at a wide range of aqueous solution pH's from about 1 to about 12 or 13.

The temperature of the cell 10 in operation can vary from about 0° to about 120° C., with a preferred temperature range being from about 5° to about 95° C. The aqueous solution feed stream can be preheated to increase the operating temperature, if necessary. The cell operating current density can be from about 0.002 to about 10 KA/M², with a more preferred range being from about 0.05 to about 3 KA/M². The potential heat build-up within the cell to above the operating temperature of the cell components caused by electrical resistance limits the cell operating current density. The limiting factors affecting the current efficiency are the concentration of the oxychlorine species that is to be reduced and the mass flow rate through the high surface area cathode. The average velocity of the flow of the aqueous solution through the catholyte compartment is in the range of 0.01 to about 5.0 feet per minute, or about 0.3 to about 152 centimeters per second. The electrochemical reduction process is also adaptable for processing very slow flows on the order of grams per minute to flows greater than about 100 to about 1,000 gallons per minute.

Where an anolyte is utilized, deionized water is preferred, especially when the anode is in direct physical contact with the membrane. Other suitable anolytes that are appropriate include non-oxidizing acids in the range of about 0.5 to about 40% by weight solutions of, for example, sulfuric acid, perchloric acid and phosphoric acid. Softened water may be also be used as the anolyte, but small amounts of chloride may produce small amounts of chlorine in the output anolyte stream. Any sodium ions in the anolyte can be transferred to the catholyte, thereby forming sodium hydroxide in the solution product which might be an advantage for acid streams where there is a need to increase the pH.

A thin protective spacer material such as anode spacer 19 may be employed made from a chemically resistant plastic mesh to permit the use of expanded metal anodes. The spacer 19 can also be used to allow for gas disengagement behind the anode. Suitable materials include corrosion resistant plastics such as polyvinylidene fluoride, polyethylene, polypropylene and fluoropolymers, such as polytetrafluoroethylene.

The anode can be coated with an oxygen evolving catalytic coating such as an iridium oxide based coating on titanium, or any suitable valve or oxide forming metal that is stable as an electrode. Other suitable anode coatings can include platinum and other precious metal or oxide coatings. Perovskite based coatings made from transition metal type oxides prepared from cobalt, iron, etc. are also suitable, as is a conductive titanium oxide composition sold under the trade name of Ebonex ®.

The cathode current distributor 14 may be formed of any smooth, solid stainless steel type of material, such as types 304, 316, 310 etc. A perforated sheet could also be employed where there are no significant feed solution flows bypassing the high surface area cathode structure.

The high surface area cathode may be made from any number of suitable materials, such as graphite, carbon, nickel, stainless steel, tantalum, tin, titanium, zirconium, iron, copper, other transition metals and alloys thereof.

Precious metals, such as gold and silver, preferably in the form of coatings, could also be used. The electrode material preferably should be of the non-sacrificial type. A sacrificial type, such as an iron based material in the form of steel wool, could be used but would suffer from the disadvantage of corroding during periods of non-use or non-operation. Another sacrificial type of material is titanium, which suffers from the disadvantage of hydriding during operation. The high surface area cathode should preferably be formed of a high hydrogen overvoltage material. Materials with high hydrogen overvoltages have increased current efficiency and promote the desired reduction of the oxychlorine species to chloride. The cathode can be coated or plated with oxides, such as ruthenium or other precious metal oxides, to enhance or catalyze the electroreductive conversion of the oxychlorine species to chloride ions. Although the Examples that follow utilized a platinum plated titanium cathode current distributor, it is expected that a material having a higher hydrogen overvoltage material, such as stainless steel, would give a higher efficiency performance.

The cathode surface area is especially important with one pass or single flow through processing. The specific surface area of the cathode structure can range from about 5 cm²/cm³ to about 2000 cm²/cm³, and more preferably, from about 10 cm²/cm³ to about 1000 cm²/cm³. The high surface area density can range from about 0.5% to about 90% or more preferably from about 1% to about 80%, with an optimum range being from about 2 about 50%. The lower the density of the high surface area material, the lower is the flow pressure drop of the stream through the cathode structure.

The high surface area cathode material can be formed from any of the above-named materials in the form of felts, matted fibers, semi-sintered powders, woven cloths, foam structures or multiple layers of thin expanded or perforated sheets. The high surface area cathode can also be constructed in a gradient type of structure, that is using various fiber diameters and densities in various sections of the cathode structure to improve performance or reduce flow pressure drop through the structure. The gradient structure can also be used to enhance the current distribution through the structure. The high surface area cathode can be sintered to the cathode current distributor backplate as a unit. It is preferable to have a removable structure for ease of cathode 12 structure maintenance and replacement.

Cell 10 can be arranged also in a bipolar configuration or alternately with internal electrolyte distribution, especially where the water being treated has low conductivity. Another configuration, best seen in FIG. 2, is possible where the aqueous solution being treated may flow alternately through high surface area cathodes and low surface area anodes so that the oxyhalide species are reduced while oxygen is liberated at the anode. In this instance a cation exchange membrane is not required, but a non-conductive porous separator insulator 35 is used between the porous anode 34 and the porous cathode 32. The cell 30 has a perforated end plate 31 and is stacked in a bipolar flow-through configuration with a direction of flow being indicated by the arrow. Optimum operation of a bipolar cell of this configuration is pH dependent. Operation in the pH neutral range with anode surfaces that are catalyzed for oxygen and evolution will maximize oxygen formation and minimize reoxidation of the chloride ions.

Another alternative cell design (not shown) may be employed for low current density and high flow rate operations and is especially suitable for potable water treatment. In this design alternating layers of anode, membrane, porous cathode, cathode backplate and a plastic insulator are wrapped around an inner core. Electrical connections can be made at the core or at the outside edge of the layered roll, or both. In this design, the feed solution flows only through cathode compartment and the anode operates by oxidizing water diffused through the membrane. This design presents the advantage of preventing solution contact with the anode and re-oxidation of the reduced chloride ions to chlorine or chlorate.

In order to exemplify the results achieved, the following examples are provided without any intent to limit the scope of the instant invention to the discussion therein.

EXAMPLE I

An electrochemical cell was constructed and assembled similar to that shown in FIG. 1 consisting of an anode compartment and a cathode compartment separated by a DuPont NAFION ® 117 cation exchange membrane. The anode was an expanded titanium metal with a thin platinum electroplated coating with a titanium welded post mounted in the anode compartment in direct contact against the membrane. An expanded plastic spacer constructed of TEFLON ® polytetrafluoroethylene having a thickness of about 0.0625 inches (0.1588 cm) was used to position the anode against the membrane and to provide an anolyte liquid/gas disengagement zone behind the anode. The anode was about 3 inches (7.62 cm) by about 12 inches (30.48 cm) with a projected area of about 36 square inches (0.0232 M²).

A solid titanium platinum plated cathode current distributor plate with a welded titanium bolt connection was employed and had a thickness of about 0.030 inches (0.762 cm). The cathode was about 3 inches (7.62 cm) by about 12 inches (30.48 cm) with a projected area of 36 sq. in. (0.0232 M²). Two layers of 0.125 inch (0.13575 cm) graphite felt supplied by National Electric Carbon Company were positioned directly in contact against the cation exchange membrane and the cathode current distributor plate. The two layers of felt were compressed to the depth of the cathode compartment recess, which is approximately ⅛ of an inch (0.3175 cm) when the cell is assembled. The graphite felt layers had a specific surface area of about 300 cm²/cm³.

Deionized water was metered through a rotameter into the anode compartment at a rate of about 2 milliliters per minute. Various oxychlorine species containing aqueous solutions were metered at different flow rates into the bottom of the cathode compartment and flowed upwardly to the thickness of the high surface area graphite felt and perpendicular to the applied current. The flow rate and the applied current were varied in the tests that followed. The oxychlorine species concentrations were analyzed in the feed solutions and in the product output from the electrochemical reduction cell.

The attached Table I gives the results of 3 tests demonstrating the direct reduction of dilute sodium chlorite and deionized water being processed in a single flow through arrangement.

Test set 1 shows the results of processing a 100 ppm sodium chlorite solution at about a 2 ampere setting with a constant mass flow rate of about 53 grams per minute. Sodium chlorite in the product was reduced to about 51 to about 56 ppm at about 2.0 amperes with the current efficiency of about 8.4 to about 9.1%. At a reduced current of about 1.0 amperes, the sodium chlorite concentration slightly increased to about 53 to about 61 ppm with a higher current efficiency of 39 to about 46.6%.

Test set 2 in Table I employed a slightly higher concentration of about 107 ppm of sodium chlorite and deionized water in a similar one pass flow through reduction treatment. Both the flow rate and current were varied with the results as shown in Table I. The lower flow rate of about 27.6 grams per minute and a lower amperage of about 1.0 amps yielded a 58% reduction in chlorite and current efficiency of about 12.2%. The highest chlorite reduction occurred at 27.6 grams per minute flow rate at 4 amps, yielding about a 73.9 to 76.3% chlorite product solution reduction to about 25 to about 28 ppm.

Test set 3 in Table I used the product solution obtained from Test set 2 and had it recycled with about 51 ppm sodium chlorite. A chlorite reduction of about 56.1 to about 60%, effectively about 20-22 ppm, was obtained at a solution flow rate of about 53 grams per minute and 2 amps.

The attached Table II shows the test results employing a higher concentration of dilute sodium chlorite dissolved in deionized water processed multiple times through the cell at a single pass flow arrangement. Test set 1 used a feed concentration of about 1078 ppm sodium chloride that was passed through the cell at a flow rate of about 55 grams per minute and at a current of about 4.0 amperes. In the first pass the chlorite in the product stream was reduced by about 34.7% to 704 ppm. After the second pass through the cell, the chlorite was reduced by a total of 53.7% from the original concentration to about 499 ppm. In the third pass, the concentration was reduced by a total of 66.3% to about 363 ppm, while in the fourth pass the concentration was reduced by a total of 77.9% to about 238 ppm. The cell current efficiency ranged between about 12.2 and 36.6% under these operating conditions.

Table 3 shows the test results of two test sets demonstrating the direct reduction of dilute chlorine dioxide solution in tap water. The water contained about 6.7 ppm chlorine dioxide and about 2 ppm of chlorine that was processed through the cell on a single pass. The Test set 1 analysis was reported as a total titration as NaClO₂. The results with the chlorine dioxide/chlorine tap water solution showed about an 80% total reduction as sodium chlorine dioxide at about 2.00 amperes of a flow rate of about 53 grams per minute. The chlorine dioxide was reduced from about 11.3 ppm to about 2.2 ppm.

In the second test set the feed from test set 1 was diluted by about half so that the chlorine dioxide was reduced from about 6.6 ppm to about 2.2 ppm at a flow rate of about 53 grams per minute and a current of about 0.5 amps.

TABLE I

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORITE IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Graphite Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLUTION TITRATION ml	gm Sample	PRODUCT SOLUTION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUCTION %
TEST SET #1: Sodium Chlorite in Deionized Water Solution - Dilute Solution										
FEED COMPOSITION →				8.50	1.80	40.816	0.100	100		
1:15	53.0	2.00	← Cell Start-up							
1:25	53.0	2.00	2.83	9.72	1.10	47.955	0.052	52	9.1	48.0
1:35	53.0	2.00	2.81	9.74	0.90	40.027	0.051	51	9.2	49.0
1:40	53.0	2.00	2.79	9.66	1.00	40.645	0.056	56	8.3	44.2
1:45	53.0	2.00	2.79	9.62	1.00	40.908	0.055	55	8.4	44.6
1:50	53.0	1.00	← Change in Current							
1:55	53.0	1.00	2.55	8.98	1.10	41.226	0.061	61	14.9	39.5
2:00	53.0	1.00	2.55	9.01	1.00	40.339	0.056	56	16.5	43.8
2:10	53.0	1.00	2.55	9.10	1.00	40.485	0.056	56	16.6	44.0
2:15	53.0	1.00	2.55	9.10	0.95	40.340	0.053	53	17.6	46.6
TEST SET #2: Sodium Chlorite in Deionized Water Solution - Dilute Solution										
FEED COMPOSITION →				8.50	1.90	40.421	0.107	107		
2:30	27.6	1.00	← Cell Start-up on New Feed							
2:35	27.6	1.00	2.63	9.70	0.80	40.777	0.045	45	12.2	58.3
2:40	27.6	1.00	2.63	9.66	0.80	40.748	0.045	45	12.2	58.2
2:40	27.6	2.00	← Change in Current							
2:45	27.6	2.00	2.83	10.12	0.70	41.488	0.038	38	6.7	64.1
3:00	27.6	2.00	2.81	9.98	0.70	41.021	0.039	39	6.7	63.7
3:05	27.6	4.00	← Change in Current							
3:10	27.6	4.00	3.17	10.35	0.45	40.371	0.025	25	4.0	76.3
3:15	27.6	4.00	3.12	10.27	0.50	40.732	0.028	28	3.9	73.9
3:15	53.0		← Change in Flowrate							
3:25	53.0	4.00	3.12	9.86	0.90	40.346	0.051	51	5.3	52.5
3:30	53.0	4.00	3.12	9.83	0.90	41.906	0.049	49	5.5	54.3
3:30	53.0	6.00	← Change in Current							
3:35	53.0	6.00	3.33	10.03	0.85	41.542	0.046	46	3.8	56.5
3:40	53.0	6.00	3.33	9.87	0.85	41.544	0.046	46	3.8	56.5
TEST SET #3: Product Solution from Test Set #2 Used as Feed										
FEED COMPOSITION →				9.75	0.90	40.437	0.051	51		
3:50	53.0	2.00	← Cell Start-up on New Feed							
4:00	53.0	2.00	2.75	9.14	0.40	40.947	0.022	22	5.3	56.1
4:10	53.0	2.00	2.75	9.30	0.40	44.889	0.020	20	5.7	60.0

TABLE II

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORITE IN A SINGLE PASS ELECTROCHEMICAL CELL
— RECYCLE TESTS —
CATHODE: Graphite Felt

	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLUTION TITRATION ml	gm Sample	PRODUCT SOLUTION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 % REDUCTION PER PASS	NaClO2 % REDUCTION CUMULATIVE
TEST SET #1: Sodium Chlorite in Deionized Water Solution - Dilute Solution											
FEED COMPOSITION →			—		4.75	10.000	1.078	1078			
	55.0	4.00	← Cell Start-up								
1st PASS	55.0	4.00	2.60	—	3.10	10.000	0.704	704	20.0	34.7	34.7
→	1st Pass Solution Product used as Feed through Cell Again										
2nd PASS	55.0	4.00	2.60	—	2.20	10.000	0.499	499	20.0	29.0	66.3
→	2nd Pass Solution Product used as Feed through Cell Again										
3rd PASS	55.0	4.00	2.60	—	1.60	10.000	0.363	363	13.3	27.3	66.3
→	3rd Pass Solution Product used as Feed through Cell Again										
4th PASS	55.0	4.00	2.60	—	1.05	10.000	0.238	238	12.2	34.4	77.9

TABLE III

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORINE DIOXIDE IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Graphite Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLUTION TITRATION ml	gm Sample	PRODUCT SOLUTION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUCTION %

TEST SET #1: Chlorine Dioxide in Tap Water Solution - Dilute Solution

TABLE III-continued

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORINE DIOXIDE
IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Graphite Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLU-TION TITRATION ml	gm Sample	PRODUCT SOLU-TION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUC-TION %
				ClO2 concentration is 0.0067 gpl or 6.7 ppm						
	FEED COMPOSITION →			6.22	0.40	80.552	0.0113	11.3		
4:15	53.0	2.00	← Cell Start-up							
4:25	53.0	2.00	2.72	6.78	0.08	80.608	0.0023	2.3	1.7	80.0
4:30	53.0	2.00	2.72	6.65	0.08	80.957	0.0022	2.2	1.7	80.1
4:35	53.0	2.00	2.72	6.50	0.08	81.137	0.0022	2.2	1.7	80.1
4:35	53.0	0.50	← Change in Current							
4:40	53.0	0.50	2.39	6.30	0.12	80.623	0.0034	3.4	6.0	70.0
4:45	53.0	0.50	2.39	5.96	0.08	81.044	0.0022	2.2	6.8	80.1
4:50	53.0	0.50	2.39	5.81	0.08	83.021	0.0022	2.2	6.8	80.6
	TEST SET #2: Chlorine Dioxide in Tap Water Solution - Feed from Test Set #4 Diluted by ⅛									
	FEED COMPOSITION →			6.74	0.24	83.143	0.0066	6.6		
4:50	53.0	0.50	← Cell Start-up							
5:00	53.0	0.50	2.40	6.35	0.08	80.181	0.0023	2.3	6.8	65.4
5:10	53.0	0.50	2.40	6.32	0.08	81.182	0.0022	2.2	6.8	65.9
5:10	53.0	2.00	← Change in Current							
5:20	53.0	2.00	2.79	7.20	0.08	82.051	0.0022	2.2	1.7	66.2
5:25	53.0	2.00	2.80	7.25	0.08	81.688	0.0022	2.2	1.7	66.1

EXAMPLE II

The same electrochemical cell as was utilized in Example I was assembled, except that the high surface area cathode was made from 316L stainless steel felt which was compressed to the depth of the cathode compartment recess.

The attached Table IV gives the results of a series of runs under Test set 1 that demonstrates the direct reduction of dilute sodium chlorite dissolved in deionized water and processed in a single pass through flow method. A dilute 102 ppm sodium chlorite solution was processed at three different ampere settings at mass flow rates of 53 gm/min for settings of 2.0 amperes, 0.50 amperes and 0.25 amperes. The 2.0 ampere settings produced about a 78% reduction to about 22-23 ppm at 15% current efficiency. At the lower 0.50 ampere setting, the chlorite concentration in the product solution increased to about 34 ppm, but with a much higher current efficiency of about 51.5%. Lowering the applied current further to about 0.25 amperes increased the chlorite in the product to about 42-43 ppm, but at a higher current efficiency of about 88.9-90.8%.

Lowering the flow rate to about 26.5 gm/min at an applied current of about 0.50 amperes, the chlorite in the product solution was reduced substantially to about 17-19 ppm at a current efficiency of about 31.3-31.5%.

The attached Table V gives the results of three runs made in the same cell with very dilute sodium chlorite dissolved in deionized water and processed in a single pass through flow method. About 8.8 ppm sodium chlorite solution was processed with a constant flow rate of about 53 gm/min at ampere settings of about 0.10, 0.50 and 1.00 amperes.

At an applied current of about 0.5 amperes, the sodium chlorite solution was reduced by about 90.4-90.6% to about 0.8 ppm at a current efficiency of about 6%. At the lower applied current setting of about 0.10 amperes, the chlorite concentration in the product increased to about 1.5 ppm, but with a higher current efficiency of about 27%. Raising the applied current setting to about 1.0 amperes, the sodium chlorite concentration in the product solution was substantially reduced to no detectable amount, with an analysis detection limit of about 0.5 ppm.

This Example shows the higher efficiency of the stainless steel felt over the graphite felt.

TABLE IV

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORITE
IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Stainless 316L Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLU-TION TITRATION ml	gm Sample	PRODUCT SOLU-TION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUC-TION %
	TEST SET #1: Sodium Chlorite in Deionized Water Solution - Dilute Solution									
	FEED COMPOSITION →			8.67	2.70	60.004	0.102	102		
2:50	53.0	2.00	← Cell Start-up							
3:05	53.0	2.00	3.03	10.03	0.60	60.575	0.022	22	15.0	78.0
3:15	53.0	2.00	3.03	10.030	0.60	60.012	0.023	23	15.0	77.8
3:15	53.0	0.50	← Change in Current							
3:20	53.0	0.50	2.57	6.58	0.90	60.450	0.034	34	51.5	66.9
3:25	53.0	0.50	2.57	6.27	0.90	60.138	0.034	34	51.4	66.7
3:25	53.0	0.25	← Change in Current							
3:37	53.0	0.25	2.34	4.48	1.13	61.147	0.042	42	90.8	58.9
3:45	53.0	0.25	2.34	4.70	1.17	61.513	0.043	43	88.9	57.7
3:45	26.5	0.50	← Change in Current & Flowrate							
3:55	26.5	0.50	2.65	9.21	0.50	60.720	0.019	19	31.5	81.7

TABLE IV-continued

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORITE
IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Stainless 316L Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLU-TION TITRATION ml	gm Sample	PRODUCT SOLU-TION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUC-TION %
4:10	26.5	0.50	2.60	9.33	0.45	61.036	0.017	17	32.2	83.6

TABLE V

ELECTROCHEMICAL REDUCTION OF AQUEOUS DILUTE SOLUTIONS OF CHLORITE
IN A SINGLE PASS ELECTROCHEMICAL CELL
CATHODE: Stainless 316L Felt

TIME	FEED FLOW-RATE (gm/min)	CELL OPERATION AMPS	VOLTS	PRODUCT pH	PRODUCT SOLU-TION TITRATION ml	gm Sample	PRODUCT SOLU-TION COMPOSITION gm/l as NaClO2	ppm as NaClO2	CELL CURRENT EFFICIENCY %	NaClO2 REDUC-TION %
TEST SET #1: Sodium Chlorite in Deionized Water Solution - Dilute Solution										
FEED COMPOSITION →				4.75	0.315	81.644	0.0088	8.8		
4:05	53.0	0.50	← Cell Start-up							
4:20	53.0	0.50	2.83	8.52	0.030	80.625	0.0008	0.8	6.0	90.4
4:25	53.0	0.50	2.83	8.60	0.030	82.306	0.0008	0.8	6.0	90.6
4:25	53.0	1.00	← Change in Current							
4:35	53.0	1.00	2.57	9.10	0.000	60.450	0.0000	0.0	3.3	100.0
4:40	53.0	1.00	2.57	9.08	0.000	60.138	0.0000	0.0	3.3	100.0
4:40	53.0	0.10	← Change in Current							
3:45	53.0	0.10	2.43	6.20	0.040	61.147	0.0015	1.5	27.4	83.0
4:55	53.0	0.10	2.43	6.18	0.040	61.513	0.0015	1.5	27.5	83.1

The scope of the intended claims is intended to encompass all obvious changes in the details, materials, and arrangements of parts, which will occur to one of skill in the art upon a reading of the disclosure. For example, while the reduction has primarily been described as occurring in an aqueous feed solution that is reduced in a single pass through the cell 10, it is possible to recycle the feed solution multiple times to increase the desired reduction, as was done in Test set 3 of Example I in the data presented in Table I. It is also possible to add salts, such as anions of chlorides, sulfates, phosphates or carbonates, to the feed solution to increase the efficiency of the high surface area cathodes.

Having thus described the invention, what is claimed is:

1. A process for electrochemically treating an aqueous solution containing inorganic oxyhalide species, comprising the steps of:

(a) positioning a separator between an anode and a cathode and directly against at least the cathode in an electrochemical reduction cell to thereby separate a catholyte compartment from an anolyte compartment;

(b) feeding the aqueous solution into the catholyte compartment of the electrochemical reduction cell so that the only flow direction through the catholyte compartment is parallel to the separator and normal to electrical current flow;

(c) utilizing a high surface area, high hydrogen overvoltage cathode to electrochemically reduce substantially all of the oxyhalide species in the aqueous solution in the catholyte compartment to halide ions to produce a purified product of water having halide ions, hydrogen gas if any, and a lesser quantity of oxyhalide species; and

(d) separating any hydrogen gas from the product stream.

2. The process according to claim 1 further comprising feeding aqueous solutions having low concentrations of oxyhalides to the catholyte compartment

3. The process according to claim 1 further comprising feeding an aqueous solution having a pH of between about 2 and about 13 to the catholyte compartment.

4. The process according to claim 3 further comprising feeding an aqueous solution having the oxychlorine species selected from the group consisting of hypochlorous acid, chlorine dioxide, chlorites, chlorates and perchlorates to the catholyte compartment.

5. The process according to claim 3 further comprising removing trace transition metal ions from the aqueous solution by depositing them on the high surface area cathode.

6. The process according to claim 5 further comprising periodically acid treating the cathode to remove built up deposits of the trace transition metals and any alkaline earth salt deposits.

7. The process according to claim 3 further comprising using an anode that is placed against the separator.

8. The process according to claim 4 further comprising first treating the aqueous solution with chlorine dioxide as part of a potable water treatment process prior to feeding the aqueous solution into the electrochemical reduction cell.

9. The process according to claim 4 further comprising treating the aqueous solution as part of a waste water treatment process that has been treated with chlorine dioxide to remove unreacted and by-product chlorate and chlorite byproduct prior to feeding the aqueous solution into the electrochemical reduction cell.

10. The process according to claim 1 further comprising electrochemically reducing substantially all of the oxyhalide species in the catholyte compartment to the halide ion to produce a purified product of water having less than 30 parts per million oxyhalide species.

11. The process according to claim 10 further comprising electrochemically reducing substantially all of the oxyhalide species in the catholyte compartment to the halide ion to produce a purified product of water having less than 0.5 parts per million oxyhalide species.

12. The process according to claim 1 further comprising feeding a dilute electrolyte selected from the group consisting of deionized water, softened water and non-oxidizable acids to the anolyte compartment.

13. The process according to claim 12 further comprising electrochemically oxidizing the dilute electrolyte in the anolyte compartment to produce oxygen.

14. The process according to claim 11 further comprising using a cation exchange membrane as the separator.

15. The process according to claim 1 further comprising using a diaphragm as the separator.

16. A process for electrochemically treating an aqueous solution containing inorganic oxyhalide species, comprising the steps of:

(a) positioning a separator between an anode and a cathode and directly against at least the cathode in an electrochemical reduction cell to thereby separate a catholyte compartment from an anolyte compartment;

(b) feeding the aqueous solution into the catholyte compartment of the electrochemical reduction cell so that the only flow direction through the catholyte compartment is parallel to the separator and normal to electrical current flow;

(c) utilizing a high surface area cathode to electrochemically reduce at high efficiency substantially all of the oxyhalide species in the aqueous solution in the catholyte compartment to the halide ion to produce a purified water product having halide ions, hydrogen gas if any, and residual oxyhalide species, the high efficiency reduction being characterized by having a current efficiency and an oxyhalide removal efficiency whose sum is greater than 50%; and

(d) separating any hydrogen gas from the product stream.

17. The process according to claim 16 further comprising feeding a dilute electrolyte selected from the group consisting of deionized water, softened water and non-oxidizable acids to the anolyte compartment.

18. The process according to claim 17 further comprising electrochemically oxidizing the dilute electrolyte in the anolyte compartment to produce oxygen.

19. The process according to claim 18 further comprising feeding aqueous solutions having low concentrations of oxyhalides to the catholyte compartment.

20. The process according to claim 19 further comprising feeding an aqueous solution having a pH of between about 2 and about 13 to the catholyte compartment.

21. The process according to claim 20 further comprising feeding an aqueous solution having the oxychlorine species selected from the group consisting of hypo-

chlorous acid, chlorine dioxide, chlorites, chlorates and perchlorates to the catholyte compartment.

22. The process according to claim 21 further comprising first treating the aqueous solution with chlorine dioxide as part of a potable water treatment process prior to feeding the aqueous solution into the electrochemical reduction cell.

23. The process according to claim 21 further comprising treating the aqueous solution as part of a waste water treatment process that has been treated with chlorine dioxide to remove unreacted and byproduct chlorate and chlorite by-product prior to feeding the aqueous solution into the electrochemical reduction cell.

24. The process according to claim 22 further comprising electrochemically reducing substantially all of the oxyhalide species in the catholyte compartment to the halide ion to produce a purified product of water having less than 30 parts per million oxyhalide species.

25. The process according to claim 24 further comprising electrochemically reducing substantially all of the oxyhalide species in the catholyte compartment to the halide ion to produce a purified product of water having less than 0.5 parts per million oxyhalide species.

26. The process according to claim 25 further comprising using a cation exchange membrane as the separator.

27. The process according to claim 25 further comprising using a diaphragm as the separator.

28. A process for electrochemically treating an aqueous solution containing inorganic oxyhalide species, comprising the steps of:

(a) feeding the aqueous solution into a catholyte compartment of an electrochemical reduction cell having a separator separating a cathode in the catholyte compartment from an anode in an anolyte compartment so that the aqueous solution substantially only flows lengthwise through the cathode and normal to the electrical current flow;

(b) utilizing a high surface area cathode to electrochemically reduce at high efficiency substantially all of the oxyhalide species in the aqueous solution in the catholyte compartment to the halide ion to produce a purified water product having halide ions, hydrogen gas if any, and residual oxyhalide species, the high efficiency reduction being characterized by having a current efficiency and an oxyhalide removal efficiency whose sum is greater than 50%; and

(c) separating any hydrogen gas from the product stream.

29. The process according to claim 28 further comprising feeding an aqueous solution having oxychlorine species selected from the group consisting of hypochlorous acid, chlorine dioxide, chlorites, chlorates and perchlorates to the catholyte compartment.

30. The process according to claim 29 further comprising feeding a dilute electrolyte selected from the group consisting of deionized water, softened water and non-oxidizable acids to the anolyte compartment.

* * * * *

Process for the Purification of Aqueous Solutions Polluted by Nitrate Ions
Patent Number: 5,266,201
Date of Patent: November 30, 1993
Assignee: Lafarge Fondu International, Neuilly sur Seine, France

United States Patent [19]

Letourneux et al.

[54] **PROCESS FOR THE PURIFICATION OF AQUEOUS SOLUTIONS POLLUTED BY NITRATE IONS**

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[30] **Foreign Application Priority Data**

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[58] Field of Search 210/620, 631, 702, 714, 210/726, 730, 731, 734, 738, 724; 423/115, 119, 122, 125, 127, 395, 397

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[57] **ABSTRACT**

The invention relates to a process for the purification of aqueous solutions polluted by nitrate ions. This process is characterised in that it consists in precipitating hydrated double or mixed calcium nitroaluminates, such as, in particular, hydrated calcium mononitroaluminate, by adding at least one agent supplying the element aluminium and at least one agent supplying the element calcium to the solutions to be treated, the overall mole ratio of the element aluminium to nitrate, Al/NO3, being superior to 1 and the overall mole ratio of calcium to nitrate, Ca/NO3, being superior to 2, and in that the precipitation reaction is performed with stirring and at a basic pH, preferably above 10.5.

The process according to the invention is intende, in particular, to the treatment of polluted waters such as municipal waste water and factory effluents and to the treatment of liquid manure.

32 Claims, No Drawings

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PROCESS FOR THE PURIFICATION OF AQUEOUS SOLUTIONS POLLUTED BY NITRATE IONS

This application is a continuation of application Ser. No. 07/817,808, filed Jan. 8, 1992, abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a process for the purification of aqueous solutions polluted by nitrate ions.

The invention also relates to recycling of the solid compounds emanating from the above-mentioned purification process, preferably in the field of fertilizers when the bound nitrate content is sufficient.

Nitric acid is one the most widely used mineral acids. Nitric acid is used on a very large scale in the chemical industry, predominantly for the manufacture of artificial fertilizers, particular in the form of ammonium nitrate. Nitric acid, in addition, is of very great importance in the synthesis of many explosives.

The salts of nitric acid, nitrates, are also well known and widely used in the chemical and metallurgical industries.

The use of nitric acid or its salts is accompanied, in most cases, by the discharge of effluents containing nitrate ions. Industrial facilities also discharges various other forms of nitrogen which may be converted into nitrates: ammoniacal nitrogen is discharged, in particular by coking plants, and nitrogenous organic compounds are discharged, in particular, by the agri-food-stuffs plants.

Nitrates can have a natural origin, such as in the form of deposits of salts, generally of sodium nitrate.

Nitrates can also emanate from the conversion of ammoniacal nitrogen by biochemical nitrification. Liquid manure constitutes one of the raw materials richest in ammoniacal nitrogen: approximately half the nitrogen present in liquid manure is in organic form, and approximately half in ammoniacal form (that is on the order of 2 to 3.5 g/l of NH_4^+). In smaller proportions, municipal waste water also contains ammoniacal nitrogen which can likewise be converted into nitrates biochemically.

To accomplish nitrification biochemically, it can be sufficient to aerate the liquid manure when the latter naturally contains the appropriate bacteria. The nitrogen present in liquid manure is modified to only slightly during storage of the liquid manure; at the very most, a slight loss takes place through outgassing of ammonia. Spreading on the ground causes mineralization of the readily decomposable organic matter and nitrification of NH_4^+. The nitrates produced may be used by plants, assimilated by microorganisms or leached in depth into the soil beyond the root absorption zone; they are then lost to the plant and contribute, to long or short term pollution of groundwater.

Whether of synthetic or natural origin and irrespective of the chemical nature of the counter anion, nitrates are, for the most part, soluble in aqueous media in high proportions. As an example, solubility in water of calcium nitrate, $Ca(NO_3)_2$, reaches 1.212 kg per liter at 18° C. and that of sodium nitrate, $NaNO_3$, reaches 0.921 kg per liter at 25° C.

The presence of ever increasing amounts of nitrates in the natural environment constitutes a matter growing of concern. It is known that, taken in repeated small doses, nitrates are potentially toxic due to the possible conver-

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sion of nitrates to nitrates, which can cause fatal methemoglobinemia in young children, and to nitrosamines, which are reputedly carcinogenic. For this reason, doctors recommend giving only water free from nitrate ions to young children. In point of fact, as a result of their high solubility in aqueous media, the concentration of nitrates, whether they originate from discharges of industrial effluents, from municipal waste water or from chemical or natural fertilizers (spreading of liquid manure), is gradually increasing in surface water and groundwater which, in some instances, has become unfit for human consumption.

The nitrate concentration is limited to 50 mg per liter in drinking water in France and in the European Community in general. However, as a result of the lack of a purification plant suited to the removal of nitrates on French territory, nitrate ion concentrations which can range up to 100 mg per liter can be found in some drinking water supplied to the water.

To solve this problem, various purification processes are currently in use for the treatment of water intended for human consumption. However, no economically advantageous process that can be implemented on an industrial scale exists for the treatment of effluents highly polluted with nitrates, such as liquid manure.

One type of process used for obtaining drinking water by physicochemical means involves the removal of nitrate ions by denitration with an ion exchange resin. This process requires water possessing a content of suspended solid matter of less than 1 mg per liter; otherwise, the water to be treated must first be subjected to sieving, followed by one or more flocculation, filtration and/or settling, and physical separation, operations.

The ion exchange resin retains the nitrate ions, as well as sulfate ions, chloride ions and hydrogencarbonate ions.

A main drawback of this process is that it cannot be used if there is an excessive amount of ions and chloride ions in the water, which have affinities which are, respectively, much greater than and similar to that of nitrates for the resins. Since regeneration of the resins is generally carried out with sodium chloride, a replacement of the nitrate ions by chloride ions takes place during the purification process. This results in an increase in the chloride ion content in the water treated by this process. Another major drawback of this process involves the disposal of the eluates which are rich in chlorides, nitrates, and often sulfates, obtained after regeneration of the resins. If the concentrations are not too high, they go into the nearest stream. In the other cases, they are either sent to the nearest biological purification plant or stored.

In another type of biological process, nitrate ions are removed using bound bacteria capable of metabolizing these ions. Usually, heterotrophic bacteria drawing their energy from a carbonaceous nutrient, such as ethanol or acetic acid, are used. By this process, the nitrate ions are converted into gaseous nitrogen. Proliferation of the bacteria leads to an excess of biomass or sludge, which can be treated with municipal sludges or incinerated.

This process can be used only at temperatures above 8°–10° C. In addition, these temperatures must be stable during the treatment; otherwise, control of the process is complex. This process is consequently relatively expensive to perform.

SUMMARY OF THE INVENTION

An aim of the present invention is to propose a process for the purification of aqueous solutions polluted by nitrate ions which is simple, effective and relatively inexpensive to perform.

Another aim of the invention is to recycle the compounds containing nitrate ions and resulting from this process preferably in the fertilizer sphere, without polluting the environment.

According to the invention, to achieve these aims, a process is provided for the purification of aqueous solution polluted by nitrate ions, comprising precipitating hydrated double or mixed calcium nitroaluminates, such as, in particular, hydrated calcium mononitroaluminate —3 $CaO.Al_2O_3.Ca(NO_3)_2.nH_2O$— by adding to the solutions to be treated at least one agent supplying the element aluminum, this agent being referred to as "active alumina", and at least one agent supplying the element calcium, the overall molar ratio of aluminium to nitrate, Al/NO_3, being superior to 1 and the overall molar ratio of calcium to nitrate, Ca/NO_3, being superior to 2. The precipitation reaction is performed with stirring at basic pH, preferably above 10.5, and, where appropriate, the precipitate obtained is removed, for example, by flocculation followed by one or more settling and physical separation and/or filtration operation(s).

In spite of variety of the compounds contained in the solutions to be treated, and therefore the reactions that can compete with the formation of hydrated calcium nitro-aluminate, the elimination of the nitrate ions, with the help of the invention process, is wholly satisfactory.

The process according to the invention is advantageous in more than one respect: apart from a trapping of a large proportion of the nitrate ions in the form of hydrated double or mixed calcium nitroaluminates, this process makes it possible to remove a large part of the undesirable cations in hydroxide form, as well as undesirable anions forming insoluble precipitates in the presence of the element calcium, or forming complex calcium aluminate such as carbonates, sulfates and chlorides.

Advantageously, the process according to the invention is carried out at room temperature, that is, at below 20° C. or approaching 30° C. to 40° C. according to the season. Preferably, the process according to the invention is implemented at a temperature of about 20° C., and more preferably at a temperature less than 20° C. Under those conditions, although the starting kinetic of the reaction is slower, on the other hand, the yields at those temperatures are better.

Where appropriate, prior to separation of the nitrate ions, various chemical treatments may be performed to remove other undesirable compounds included in the effluent to be treated.

Where the effluents to be treated comprise suspended solid matter, it is possible to perform one or more precipitation(s) of this matter by flocculation, for example, using an addition of ferric chloride and a base, or using aluminum sulfate, or alternatively using an organic flocculating agent, such as polyacrylamides, this precipitation being followed by one or more filtration operation(s) and/or settling and physical separation operation(s).

Where the effluents to be treated comprise undesirable anions or components forming insoluble calcium salts, precipitation of these components is advanta-

geously performed by adding an agent supplying the element calcium, and the precipitated phases obtained are then removed before removal of the nitrates.

Preferably, this precipitation is performed using calcium hydroxide. This operation results in a lowering of the concentration of anions which are only sparingly soluble in the form of calcium salts, such as sulfates, phosphates, carbonates, fluorides, and the like. The removal of these anions makes it possible to limit the formation of other complex aluminates, concomitantly with the hydrated calcium nitroaluminates.

Where the effluents to be treated comprise undesirable cations or components forming hydroxides which are only sparingly soluble or insoluble, precipitation of these components is advantageously performed by adding a basic agent. Preferably, this precipitation is performed using calcium hydroxide. This operation results in a lowering of the concentration of anions which are only sparingly soluble in the form of calcium salts, as well as that of cations which are only sparingly soluble, such as lead, etc., in hydroxide form. After removal of the precipitated phases obtained, the the nitrates are removed.

The process according to the invention may be performed using various sources of active alumina, employed alone or in combination, for example, aluminates, particularly alkali metal aluminates; calcium aluminates constituting certain cements, such as CA_2, CA, $C_{12}A_7$; and C_3A, and calcium aluminoferrites. In the foregoing formulae and following description:

C represents CaO,

A represents Al_2O_3,

H represents H_2O.

Preferable calcium aluminates are those obtained by a sintering process rather than those obtained by a fusion process. In fact, the calcium aluminates emanating from a sintering process generally possess a better capacity for being ground as well as greater reactivity.

Hydrated calcium aluminates, such as C_4AH_{13}, can also lead to the formation of complex aluminates by ion exchange. Aluminous cements bearing the trade names FONDU, SECAR, LDSF as well as cubic-T are also suitable: the latter is a cubic calcium aluminate, C_3AH_6, decomposed thermally at approximately 300° C. to $C_{12}A_7$ and $Ca(OH)_2$. This product possesses directly the stoichiometry needed for the formation of complex aluminates ($C/A=3$) in the case of a reaction with a calcium salt.

Also preferable are, products comprising C_3A and/or $C_{12}A_7$, employed alone or in combination with other compounds with which greater reactivities as well as high yields in short periods of time, on the order of 1 to 3 hours, have been observed.

The yields are further improved when employing as reagents C_3A and CaO. The best yields and reactivities have been obtained using the reagent, which corresponds to the product produced when making of C_3A with an excess of lime.

It is preferable to work close to this theoretical stoichiometry in the first moments of formation of the calcium nitroaluminates. This stoichiometry corresponds to $C/A=4$ in the general case, and to $C/A=3$ for the treatment of a solution of a calcium salt.

The agent supplying the element calcium can be calcium hydroxide, or a calcium aluminate supplemented, if necessary, with a second agent supplying the element calcium, such as calcium hydroxide.

Advantageously, the reaction of aqueous solution polluted by nitrates according to the invention is initiated by means of addition of hydrated double or mixed calcium nitroaluminate at the beginning of the reaction in the proportion of approximately 10 to 50% by weight relative to the weight of calcium aluminate introduced.

Under these conditions, improvements have been observed in the rate of formation of hydrated double or mixed calcium nitroaluminates, principally during the initial phase of this reaction, and in the precipitation yield of the nitrates. The hydrated double or mixed calcium nitroaluminate, which is mainly to be formed during the reaction, is advantageously used as a seed.

The process according to the invention, as well as the different variants of this process described above, find an especially advantageous field of application for treating water loaded with nitrates and possibly with other inorganic compounds, such as industrial effluents and municipal waste water, as well as media loaded with ammonical nitrogen, the nitrogen being liable to be converted to nitrates such as liquid manure.

When the solution to be treated is a solution rich in nitrogen in ammoniacal form and in organic form, the present invention considerably reduces or even eliminates the pollutant power of these solutions. This applies in particular to raw materials, such as liquid manure, which generate solutions rich in nitrates through nitrification.

Liquid manure, in particular, is at present simply spread in the crude state; its high content of soluble nitrogen, chiefly in ammonium form, poses a risk of substantial pollution, especially when it is spread outside the periods of the year in which plants assimilate large amounts of nitrates needed for their growth. By means of a simple treatment of the liquid manure, prior to spreading and in accordance with the process according to the invention, the fertilizer qualities of the liquid manure are retained and/or improved while advantageously eliminating its capacity as a pollutant.

According to a first preferred embodiment of the invention, which relates especially to the treatment of solutions or suspensions comprising nitrogen in ammoniacal form, such as liquid manure, the following steps are performed successively:

1) The ammoniacal nitrogen present in the solutions to be treated is biochemically converted to nitrates in the presence of oxygen. For this purpose, the following procedure may be adopted. The solutions rich in ammoniacal nitrogen, such as liquid manure, are aerated and, if necessary, are inoculated with nitrifying microorganisms to induce nitrification.

2) Once the majority of the ammoniacal nitrogen is converted to nitrates, one or more calcium aluminates is/are added to the solution to be treated, so that the overall molar ratio of the aluminium to nitrate, Al/-NO$_3$, is superior to 1 and the overall molar ratio of the calcium to nitrate is superior to 2. If necessary, calcium hydroxide and/or another basic agent is also added to adjust the pH to a basic value, preferably to a value above 10.5, and the precipitation reaction is performed with stirring at room temperature.

3) After separation, for example, after settling has taken place or by filtration, a thick suspension or a solid is collected, which product is advantageously used as an enriching agent and fertilizer for agricultural soils.

4) Finally, a liquid effluent depleted in nitrates, the pollutant nature of which is greatly reduced in comparison with the initial liquid manure, is collected.

Thus, its discharge into the environment can be safely envisaged.

Apart from the removal of a large part of the nitrate ions, as well as ions forming insoluble hydroxides and insoluble calcium salts, the process according to the invention, in contrast to known processes, when applied to the treatment of liquid excrement, such as liquid manure, has the advantage of producing clear, decolorized and deodorized liquid effluents.

In point of fact, liquid excrement includes organic compounds of biliary origin, which are highly colored and whose coloration varies between yellow and brown hues and which, moreover, biodegrade with difficulty. It may hence be supposed that these colored organic compounds are bound in the hydrated calcium mononitroaluminate precipitate and/or the other precipitates which advantageously accompany the formation of this precipitate, namely insoluble hydroxides and insoluble calcium salts.

The alkalinity of the suspensions or solids obtained at the end of step (3) can enable an acid soil to be corrected. In addition, their content of sparingly soluble nitrate enables the nitrate fertilizer to be supplied at a rate proportional to its consumption by the plants, and thereby eliminates a source of pollution of groundwater and stream water.

In the nitrification according to step (1), ammoniacal nitrogen is biochemically converted to nitrate biochemically in the presence of nitrifying bacteria and oxygen, preferably supplied by aeration. This conversion is performed according to conventional working conditions.

It is generally accomplished in two stages by autotrophic microorganisms:

oxidation of ammoniacal nitrogen to nitrite by suitable microorganisms, e.g., microorganisms of the genus Nitrosomonas

followed by oxidation of the nitrites to nitrates by suitable microorganisms, e.g., microorganisms of the genus Nitrobacter

The nitrifying microorganisms may be found in water purification plant sludge or alternatively in partially or completely nitrified liquid manure.

The rate of nitrification depends, in particular, on the temperature; pH, which is preferably maintained at between 7.2 and 8; and the amount of oxygen which may be available to the microorganisms. It is also important to take care that the nitrification reaction medium does not contain organic or inorganic compounds capable of modifying or even inhibiting the growth of the microorganisms. For further details regarding the conditions necessary during nitrification, reference may be made to the work entitled "Mémento technique de l'eau" (Technical Handbook on Water), 9th edition, volume 1, pp. 300–301, published by DEGREMONT.

Advantageously, the adjustment to a basic pH for the requirements of the precipitation reaction of step (2) is performed using potassium hydroxide, in order to yield residual sludge rich in potassium, increasing its value as a fertilizer.

Advantageously, before the precipitation of hydrated double or mixed calcium nitroaluminates (step (2) of the first embodiment), either before or after nitrification step (1), the solid matter included in the liquid manure is at least partially separated, generally by flocculation followed by filtration and/or settling and physical separation from the solid matter, protein-rich matter, phosphates and nitrogen compounds which are only sparingly soluble in water are recovered.

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Preferably, separation of the solid matter included in the liquid manure is performed before the nitrification step (1). If this is not done, the solid matter, which possesses a certain biochemical oxygen demand (BOD), disadvantageously competes with the nitrification reaction. The filtrate constituting the clarified liquid manure is then successively subjected to:

the nitrification treatment according to step (1) where this treatment has not been carried out beforehand;

the treatment for precipitation of the nitrates in accordance with steps (2) and (3).

The best precipitation yields of the nitrates have been obtained under these conditions.

Where appropriate, the solid matter is separated from the suspension obtained at the end of step (3), for example, by flocculation followed by filtration and/or settling and physical separation. There are collected, on the one hand, a filtrate depleted in nitrates, which takes the form of a clear, practically solution capable of being spread or of being used for irrigation, and, on the other hand, solid matter containing hydrated double or mixed calcium nitroaluminates, which finds application as a fertilizer. It has, in effect, been shown by means of agronomic experiments that the nitrate ions are temporarily trapped in the solid matter in the state of hydrated double or mixed calcium nitroaluminates, but remain available to and assimilated by plants.

A practical application of the process according to the invention for the treatment of liquid manure may be envisaged according to the following example of an installation on a pig farm.

INSTALLATION OF THE PROCESS

This consists in adapting and supplementing the existing installation by partitioning the liquid manure storage tank. After adaptation and supplementation, the new installation comprises a first compartment consisting of a nitrification tank N.

The nitrification tank N is equipped with a microbubble aeration system (production of air+diffusion).

This installation also comprises a reactor for the precipitation reaction of the nitrate ions in accordance with the process according to the invention, and a salt/effluent separation system (sieve type).

The installation may be supplemented with a pretreatment of the liquid manure before nitrification (settling and physical separation, or screening and/or flocculation) with the object of reducing the BOD and hence the oxygen consumption of the medium. The flocculation may be carried out using a weakly cationic polyacrylamide.

The second compartment of the existing storage tank, referred to as tank S, is used for storing the effluent obtained after separation of the nitrate ions.

OPERATION

The average input to the installation, in m^3 of crude liquid manure per day, is dependent on the number of pigs.

The pretreatment before nitrification produces:

organic sludge having a high percentage of dry matter. These sludge contain organic nitrogen and virtually all of the phosphorus; they are used as a humous-enriching agent on the farm.

the liquid manure to be treated having a small solid matter in suspension content.

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NITRIFICATION

Feeding the nitrification tank N is carried out using liquid manure cleared of organic sludge.

The residence time is matched to the rate of nitrification.

TREATMENT

The sequences of the treatment are as follows:

At regular intervals, a certain volume V1 of nitrified liquid manure is withdrawn from the tank N to the reactor. At the same time, a certain volume V2 of nitrate-depleted final effluent may be transferred from the effluent storage tank S to the nitrification tank N in order to maintain a constant volume in the latter. The volumes V1 and V2 to be treated are then calculated so as to maintain a constant NO$_3$ concentration in the tank N and a constant level in the tank N; it enables an amount of nitrates equivalent to that formed during the period in question to be extracted from this tank.

In the reactor, the liquid manure to be treated is stirred and a suitable dose of active alumina and, if necessary, of calcium hydroxide is introduced.

The medium is kept stirring during the reaction. After the reaction, the suspension of nitrate salt is extracted from the reactor to a sieve in order to separate the salt from the effluent. It is also possible to separate the salt by a simple settling and physical separation operation.

The salt is stored while awaiting its use as a nitrogenous fertilizer. The effluent, depleted in nitrate (it generally does not contain more than 0.3 to 0.5 g/l of NO$_3$) and containing virtually all of the potassium in the liquid manure, is stored in the tank S; it is used as a fertilizer by sprinkling or by spreading.

According to a second embodiment of the invention, which is directed towards treatment of aqueous solutions comprising a high to moderate content of nitrate ions and small amounts of organic compounds such as industrial effluents or municipal waste water or regeneration solution of exchanger resins used in sewage plants, the following second variant of the process according to the invention is advantageously used:

1) One or more calcium aluminate(s) and, if necessary, calcium hydroxide and/or another basic agent to adjust the pH to a basic value, preferably to a value above 10.5, is/are added to the solution to be treated.

2) The precipitation reaction is performed with stirring and at room temperature.

3) At the end of this reaction, the suspension obtained is subjected to a settling and physical separation and/or filtration operation, after the addition of a flocculating agent where appropriate.

4) Then, if necessary, the filtrate obtained is neutralized, which also has the effect of precipitating the alumina in solution in the form of an insoluble hydroxide.

5) Lastly, the new suspension obtained is subjected to a settling and physical separation operation and/or filtration operation to obtain a purified water which can be discharged into the environment without risk of pollution.

If the nitrate content of this purified water is less than 50 mg per liter, and if it does not include other components or compounds at levels greater than those allowed in regulations, this water can be fed into drinking water distribution networks.

If the solution to be treated is a polluted water, such as a water originating from aquiculture or pisciculture

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or a municipal waste water containing ammoniacal nitrogen, an operation of nitrification of this solution, of the type presented above, is advantageously arranged.

During step (1), sodium hydroxide, potassium hydroxide or calcium hydroxide may be used as a basic agent.

Advantageously, the addition of a basic agent is performed prior to the addition of calcium aluminate. This results in a decrease in the concentration of cation which are only sparingly soluble in the form of insoluble hydroxides.

Advantageously, prior to the addition of calcium aluminate, an agent supplying the element calcium other than calcium aluminates is added to the solution to be treated. This results in a decrease in the concentration of anions which are only sparingly soluble in the form of calcium salts, such as sulfates, phosphates, carbonates, fluorides and the like.

Advantageously also, calcium hydroxide is chosen at the basic agent and agent supplying the element calcium, and is introduced prior to the calcium aluminate.

The solution then undergoes the treatment of removal of nitrate ions by precipitation after removal of the precipitated phases. These process variants enable the formation of other complex aluminates concomitantly with the mononitroaluminate to be limited.

In the precipitation steps, flocculating agents of natural origin such as alginates or xanthan gums are preferably chosen. However, salts such as ferric chloride or aluminium sulphate as well as polymers such as polyacrylamides are also suitable for the invention.

Advantageously, the residual sludges obtained in this variant of the process according to the invention at the end of step (3), when they are rich in calcium nitroaluminates, may be used as an enriching agent and fertiliser for agricultural soils. In effect, their content of sparingly soluble nitrate enables the nitrate fertiliser to be supplied at a rate proportional to its consumption by the plants, and thereby eliminates a source of pollution of groundwater and stream water. In addition, the alkalinity of these sludges can enable an acid soil to be corrected.

In the case where the filtrate is intended for the preparation of drinking water or for discharging into the environment, the filtrate [step (4)] is advantageously neutralised using CO_2 in order to precipitate calcium carbonate simultaneously with the aluminium hydroxide.

In accordance with the process according to the invention, apart from the agents needed for precipitation of the nitrates in solution, the solutions to be treated can receive crystallising agents having the property of influencing the kinetics of formation of the double or mixed nitroaluminates. These crystallising agents consist, for example, of at least one of the precipitated double or mixed nitroaluminates, taken alone or in combination.

Other features and advantages of the invention will become apparent on reading the examples which follow, given for the purpose of illustration and without implied limitation of the invention.

EXAMPLE 1 to 3

An aqueous solution containing calcium nitrate $Ca(NO_3)_2$ is introduced into a chemical reactor equipped with a magnetic stirrer: the initial NO_3 concentration varies between 500 mg per liter and 125 mg per liter. In these examples, the active alumina is calcium aluminate

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CA in aqueous solution. The additional supply of calcium is obtained by adding calcium hydroxide $Ca(OH)_2$.

The treatment is carried out by simultaneously adding CA and $Ca(OH)_2$. The treatment is carried out with stirring. The suspension obtained is filtered or treated with a flocculating agent and subjected to a settling and physical separation operation. Nitrate analysis is then performed with a specific electrode after adding a buffer and adjusting the pH to 5.5.

The other working conditions and the results for Examples 1 to 3 are recorded in Table 1 below.

TABLE I

	EXAM-PLE 1	EXAM-PLE 2	EXAM-PLE 3
Initial NO_3 concentration (mg/l)	500	125	125
Amount of CA in aqueous solution (mg/l)	2844	711	355
Amount of $Ca(OH)_2$ (mg/l)	3696	925	425
Overall mole ratio Al/NO_3	4.46	4.46	2.23
Overall mole ratio Ca/NO_3	8.93	8.92	4.71
Treatment period (min.)	15	15	15
Residual NO3, concentration (mg/l)	123	81	96
Yield (%)	75	35	23

EXAMPLES 4 to 6

The working conditions in these examples are identical to those in Examples 1 to 3, except for the agent supplying the element aluminium, which is in the form of C_3A.

The other working conditions and the results for these examples are given in Table II below:

TABLE II

	EXAM-PLE 4	EXAM-PLE 5	EXAM-PLE 6
Initial NO_3 concentration (mg/l)	500	250	2300
Amount of C_3A (mg/l)	4899	5000	5000
Amount of $Ca(OH)_2$	0	0	0
Overall mole ratio Al/NO_3	4.5	9.19	1.0
Overall mole ratio Ca/NO_3	7.25	14.28	2.0
Treatment period (min)	350 (220)	160	1100
Residual NO_3 concentration (mg/l)	86 (96)	98	480
Yield (%)	83.4 (80.8)	60.8	79.1

EXAMPLES 7 to 9

The working conditions in these examples are identical to those of Examples 1 to 3, except for the agent supplying the element aluminum, which is in the form of SECAR 71, an industrial refractory cement produced by LARARGE FONDU INTERNATIONAL. SECAR 71 is composed of approximately 70% of Al2O3, approximately 29% of CaO and various other oxides. The other working conditions and the results for these examples are given in Table III below:

TABLE III

	EXAMPLE 7	EXAMPLE 8	EXAMPLE 9
Initial NO₃ concentration (mg/l)	125	500	500
Amount of SECAR 71 (mg/l)	655	2620	2620
Amount of Ca(OH)₂ (mg/l)	1000	4000	2970
Overall mole ratio Al/NO₃	4.46	4.46	4.46
Overall mole ratio Ca/NO₃	8.91	8.91	7.19
Treatment period (min)	300	1020	1020
Residual NO3 concentration (mg/l)	78	102	169
Yield (%)	37.6%	79.6	66.2

EXAMPLES 10 and 11

The working condition in these examples are identical to those in Examples 1 to 3, except for the agent supplying the element aluminum, which is in the form of a product composed of 36% by weight of C_3A, 60% of $C_{12}A_7$, and 4% of calcium titanate. This product will be identified by M in the examples which follow.

The other working conditions and the results for these examples are given in the following Table IV:

TABLE IV

	EXAMPLE 10	EXAMPLE 11
Initial NO₃ concentration (mg/l)	500	500
Amount of M (mg/l)	4390	4390
Amount of Ca(OH)₂ (mg/l)	0	965
Overall mole ratio Al/NO₃	4.45	4.45
Overall mole ratio Ca/NO₃	5.60	7.21
Treatment period (min.)	270	75
Residual NO₃ concentration (mg/l)	186	82
Yield (%)	62.8	83.6

It is observed that the increase in the overall mole ratio Ca/NO3 by adding calcium hydroxide enables the yield to be substantially improved.

EXAMPLES 12 and 13

The working conditions in these examples are identical to those in Examples 1 to 3, except for the agent supplying the element aluminum, which is a product composed of 37% by weight of C_3A, 55% of $C_{12}A_7$ and 8% of calcium titanate. This product will be identified by N in the examples which follow.

The other working conditions and the results for these examples are given in the following Table V.

TABLE V

	EXAMPLE 12	EXAMPLE 13
Initial NO₃ concentration (mg/l)	500	500
Amount of N (mg/l)	4390	4390
Amount of Ca(OH)₂ (mg/l)	0	965
Overall mole ratio Al/NO₃	4.49	4.49
Overall mole ratio Ca/NO₃	5.58	7.19
Treatment period (min.)	540	100
Residual NO₃ concentration (mg/l)	187	98
Yield (%)	62.6	80.4

It is observed that the increase in the overall mole ratio Ca/NO₃ by adding calcium hydroxide enables the yield to be substantially improved.

EXAMPLE 14

This example relates to the treatment of liquid manure.

The test liquid manure is a porcine liquid manure.

Nitrification is performed by aeration of the manure for 72 hours, by bubbling air through it in the presence of nitrifying microorganisms.

After nitrification, this liquid manure comprises an initial nitrate concentration equal to 3000 mg/liter. The suspended solid matter is precipitated by adding aluminum sulfate in the proportion of 0.3 g/liter of manure. After separation when settling has taken place, the supernatant liquid is treated by adding an active alumina and calcium hydroxide Ca(OH)₂ to this manure with stirring during 30 minutes. The suspension obtained is filtered and the residual nitrate content is measured on the filtrate after adding a buffer of ionic strength and adjusting the pH to 5.5.

The other working conditions and the results obtained are recorded in the following Table VI:

TABLE VI

	EXAMPLE 14
Initial NO₃ concentration (mg/l)	3000
Amount of Cubic - T (mg/l)	14,182
Amount of Ca(OH)₂ (mg/l)	3582
Overall mole ratio Al/NO₃	2
Overall mole ratio Ca/NO₃	3.5
Treatment period (min.)	30
Residual NO₃ concentration (mg/l)	600
Yield (%)	80

A prior precipitation of the suspended matter, especially that of a proteinaceous nature, enabled a good denitration yield to be obtained.

EXAMPLE 15

To an aqueous solution containing calcium nitrate in the proportion of 2000 mg/l of nitrate ions, 8.78 g of the calcium aluminate identified by the letter "N" in Examples 12 and 13 and 1.93 g of Ca(OH)₂ are added per liter of solution.

Under these conditions, the overall mole ratio Al/NO₃ is equal to 2.25 and the overall mole ratio Ca/NO₃ is equal to 3.6.

The change in the pH and in the concentration of nitrates in solution is monitored as a function of the reaction time using a specific electrode after adding a buffer and adjusting the pH to 5.5.

The results of these measurements are recorded in the following Table VII:

TABLE VII

	EXAMPLE 15	
Time (min.)	(NO₃) (mg/l)	pH
15	1251	12.00
30	1065	12.03
45	1005	12.04
75	754	12.00
105	579	11.87
135	521	11.82

The yield of the precipitation reaction of the nitrate ions after 135 minute's reaction is 75%.

EXAMPLE 16

To an aqueous solution containing 1608 mg per liter of nitrate, 8.78 g per liter of the calcium aluminate identified by the letter "N" in Examples 12 and 13 and 1.93 g per liter of $Ca(OH)_2$ are added.

After five minutes' reaction, 5 g of hydrated calcium mononitroaluminate—$3CaO.Al_2O_3$. $CA(NO_3)_2$. nH_2O—containing 46% by weight of dry extract are added.

Under the conditions of this test, the overall mole ratio Al/NO_3 is equal to 2.8 and the overall mole ratio Ca/NO_3 is equal to 4.5.

The change in the pH and in the nitrate concentration is monitored as a function of the reaction time according to the method of measurement used in the previous example.

The results are recorded in the following Table VIII:

TABLE VIII

| | EXAMPLE 16 | |
Time (min.)	(NO_3) (mg/l)	pH
15	438	—
30	289	11.82
45	241	11.85
60	171	11.79
90	123	11.80
150	93	11.75

The yield of the precipitation reaction of the nitrate ions is equal to 94% after 150 minutes.

EXAMPLE 17

This example relates to a treatment of porcine liquid manure.

In a first step, a clarification of the manure is carried out by removing the solid matter. For this purpose, a flocculation is performed by adding a polyacrylamide of trade name PROSEDIM CS 284 in the proportion of 75 mg/l to precipitate the proteinaceous matter and phosphates, and the solid matter is removed after settling has taken place. The clarified supernatant is then nitrified.

Nitrification is carried out by aeration and inoculation of the liquid manure to be treated by adding a liquid manure undergoing nitrification and hence containing nitrifying microorganisms.

After nitrification, this manure includes an initial nitrate concentration equal to 2737 mg/l.

The nitrates are precipitated in the form of calcium mononitroaluminate by adding calcium aluminate identified by the letter "N" in Examples 12 and 13, as well as $Ca(OH)_2$.

At regular intervals during the reaction, the suspension obtained is filtered and the residual contents of nitrate, chloride ions, phosphate ions HPO_4^{2-} and sulphate ions SO_4^{2-} are measured on the filtrate by ion chromatography.

To carry out the precipitation, 11,853 mg/l of calcium aluminate designated by the letter "N" and 4215 mg/l of $Ca(OH)_2$ are added. Under these conditions, the overall mole ratio Al/NO_3 is equal to 2.25 and the overall mole ratio Ca/NO_3 is equal to 3.6.

The results of this test are given in the following

TABLE IX

Time (min)	Cl^- (mg/l)	NO_3^-	$HPO_4^=$	$SO_4^=$	Yield (%)
0	384	2737	204	506	—
15	342	2400	0	84	12
30	469	2018	0	0	26
45	324	1515	0	153	45
60	455	1129	0	59	59
75	448	934	0	32	66
90	262	752	0	0	72
105	405	688	0	0	75
135	224	553	0	0	80
165	399	520	0	12	81
195	213	501	0	0	82
225	195	470	0	0	83

The results of chemical analyses of the nitrified liquid manure before and after precipitation of the nitrates are given in the following Table X:

CHEMICAL ANALYSES (mg/l)

	Nitrified liquid manure before separation of the nitrates by precipitation	Final effluent obtained after precipitation of the nitrates and separation of the precipitate
Al	5.3	31.7
Ca	427.6	191.6
K	831.8	760.8
Na	148.4	150.8
Cu	3	0.035
Zn	12.5	nd*
Ni	0.21	0.01
Pb	0.09	nd*
W	0.09	nd*
Co	0.06	nd*
CD	0.06	nd*
NO_3	2737	470
NH_4	nd*	nd*
Cl	384	195
P_2O_5	89	nd*
SO_4	506	nd*
pH	5.8	12.2
		Analysis of the precipitate (weight %)
Al_2O_3		18.00
CaO		39.71
K_2O		0.26
Na_2O		nd*
NO_3		9.14
H_2O		31.71

*nd means non-detectable

Apart from a substantial removal of the nitrates by means of the process according to the invention, it will be noted that the proportions of the elements Cu and Zn in the effluent are quite negligible. These elements are, in effect, advantageously bound in the precipitate.

The final effluent, depleted in nitrates, may be spread in nature without risk of pollution. The nitrate-rich precipitate is advantageously used as fertilizer, and spread at the time when the growth of the plants requires a supply of nitrogen.

EXAMPLE 18 AND 19

An aqueous solution containing calcium nitrate $Ca(NO_3)_2$ at a concentration of 125 mg/l of nitrate ions is introduced into a chemical reactor equipped with a magnetic stirrer. The agent supplying the element aluminum is sodium aluminate $NaAlO_2$ in aqueous solution. The additional supply of calcium is provided by adding calcium hydroxide $Ca(OH)_2$.

The treatment is carried out by simultaneously adding NaAlO$_2$ and Ca(OH)$_2$. The treatment is carried out with stirring. The suspension obtained is filtered or treated with a flocculating agent and subjected to a settling and physical separation operation. The nitrate analysis is performed with a specific electrode.

The other working conditions and the results from these examples are given in the following Table XI.

TABLE XI

	EXAMPLE 18	EXAMPLE 19
Initial NO$_3$ (mg/l)	125	125
NaAlO$_2$ in the solution (mg/l)	2950	1475
Ca(OH)2 (mg/l)	5255	2590
Mole ratio Ca/NO$_3$	35	17.5
Mole ratio Al/NO$_3$	18	9
Treatment period (min)	15	15
Residual NO$_3$ (mg/l)	62	114
Yield (%)	50	8

EXAMPLES 20 TO 21

A reagent to eliminate nitrate ions in the state of hydrated calcium nitroaluminate, double or mixed, is added to an aqueous solution containing 300 mg/liter of nitrate and corresponding to the supernatant liquid obtained after nitrification and precipitation of the suspended solid matter of the manure presented in Example 14.

After reaction, the obtained suspension filtered and the residual nitrate content is measured on the filtrate.

The other working condition and the obtained results are reported in the following Table XII.

TABLE XI

	EXAMPLE 20	EXAMPLE 21
Amount of added pure C3A (mg/l)	29.7	0
Amount of added Ca(OH)2 (mg/l)	3.5	0
Amount of added C4A(C3A.CaO)	0	35.3
Overall mole ratio Al/NO$_3$ (mg/l)	2	2
Overall mole ratio Ca/NO3	3.5	4
Treatment period (min)	180	90
Residual NO$_3$ concentration (mg/l)	572	410
Yield (%)	81	86

EXAMPLES 22 TO 24

Aqueous solution polluted by nitrate ions and other ions are purified by using the reagent identified by "M" in Examples 10 and 11.

Examples 22 to 24 have been made with aqueous solution containing, before treatment, a majority of 3 g/l of NO3.

The purification method is the same for each of these examples, that is:

overall mole ratio Al/NO3=2

overall mole ratio Ca/No3=4.

In the following Table XIII arc reported the other ions which are in high proportion in the solution to be treated as well as the purification results.

Example	Nature of the ions Y in high proportion	Amount of Y (mg/l)	Treatment period (mg/l)	Yield of epuration in NO3	Yield of epuration in Y
22	Chloride	1000	120	70%	52%
23	Phosphate	1000	120	78%	100%
24	Sulfate	1000	120	68%	99%

The entire disclosure of all applications, patents, and publications, cited above and below, and of corresponding French Application 91/00260, are hereby incorporated by reference.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. A process for the purification of aqueous solutions polluted by nitrate ions, comprising precipitating hydrated double or mixed calcium nitroaluminates, by adding to the solutions to be treated at least one agent supplying the element aluminum and at least one agent supplying the element calcium, the overall mole ratio of the element aluminum to nitrate, Al/NO$_3$, being higher than 1 and the overall mole ratio of calcium to nitrate, Ca/NO$_3$, being higher than 2, and conducting the precipitation reaction with stirring at basic pH.

2. A process according to claim 1, wherein the calcium nitroaluminate is hydrated calcium mononitroaluminate.

3. A process according to claim 1, wherein the precipitation reaction is performed at room temperature, about 20°–25° C.

4. A process according to claim 1, wherein the precipitation reaction is performed at a pH above 10.5.

5. A process according to claim 1, wherein the agent supplying the element aluminum is an alkali metal aluminate.

6. A process according to claim 1, wherein the agent supplying the element aluminum is a calcium aluminate.

7. A process according to claim 2, wherein the agent supplying the element aluminum is a calcium aluminate.

8. A process according to claim 6, wherein the agent supplying the element aluminum comprises at least one of (CaO)$_3$Al$_2$O$_3$ and (CaO)$_{12}$(Al$_2$O$_3$)$_7$.

9. A process for the treatment of solutions and suspensions containing nitrogen in ammoniacal form, said solution optionally containing solid matter, wherein the following steps are performed successively:

(1) the conversion to nitrates of the ammoniacal nitrogen present in the solutions to be treated is performed biochemically in the presence of nitrifying bacteria and oxygen;

(2) then, once the majority of the ammoniacal nitrogen is converted to nitrates, at least one calcium aluminate is added to the solution to be treated, so that the overall mole ratio of the element aluminum to nitrate, Al/NO$_3$, is higher than 1 and that the overall mole ratio of the element calcium to nitrate is higher than 2, and, optionally, a basic agent is

added to adjust the pH to a basic value, and the precipitation reaction is performed with stirring and at room temperature;

(3) after separation, a thick suspension or a solid is collected, which is suitable as an enriching agent and fertilizer for agricultural soils; and

(4) finally, a liquid effluent depleted in nitrates is collected.

10. A process according to claim 9, wherein the solution to be treated is brought to a basic pH by adding potassium hydroxide.

11. A process according to claim 9, wherein said solution contains solid matter and before the precipitation of hydrated double or mixed calcium nitroaluminates, either before or after the nitrification step (1), the solid matter included in the solution to be treated is separated at least partially from the solution.

12. A process according to claim 11, wherein the separation is conducted by flocculation followed by a filtration operation and/or settling.

13. A process according to claim 11, wherein the separation of the solid matter is performed before the nitrification step (1).

14. A process according to claim 1, wherein the solution to be treated is a water polluted with nitrates, comprising adding to the solution to be treated:

(1) at least one calcium aluminate and, optionally, a basic agent to adjust the pH to a basic value, such that the mole ratio of the element aluminum to nitrate, Al/NO_3, is higher than 1 and that the overall mole ratio of calcium to nitrate, Ca/NO_3, is higher than 2;

(2) conducting the precipitation reaction with stirring and at room temperature;

(3) after the precipitation reaction, subjecting resultant suspension to a separation step to remove solids from the solution;

(4) optionally, neutralizing resultant solidsdepleted solution to precipitate the aluminum in solution in the form of an insoluble hydroxide; and

(5) separating resultant insoluble hydroxide from the resultant suspension to obtain a purified water which can be discharged into the environment.

15. A process according to claim 14, wherein the solution to be treated is a polluted water originating from agriculture or a municipal waste water containing water-soluble compounds containing ammoniacal nitrogen and wherein, prior to removal of the nitrates, the solution is subjected to nitrification.

16. A process according to claim 14, wherein prior to adding of calcium aluminate, a basic agent is added to decrease the concentration of cations which are only sparingly soluble in the form of hydroxides.

17. A process according to claim 14, wherein prior to the addition of calcium aluminate, an agent supplying the element calcium is added to decrease the concentration of anions which are only sparingly soluble in the form of calcium salts.

18. A process according to claim 16, wherein prior to the addition of calcium aluminate, an agent supplying the element calcium is added to decrease the concentration of anions which are only sparingly soluble in the form of calcium salts.

19. A process according to claim 18, wherein the anions which are only sparingly soluble in the form of calcium salts and the cations which are only sparingly soluble in the form of hydroxides are decreased simultaneously by adding calcium hydroxide.

20. A process according to claim 14, wherein the solution obtained at the end of step (4) is neutralized with CO_2.

21. A process according to claim 1, wherein the solution to be treated is selected from municipal wastewater and industrial effluents.

22. A process according to claim 9, wherein the solution to be treated is liquid manure.

23. A process according to claim 3, wherein the precipitation reaction is conducted at about 20° C.

24. A process according to claim 9, wherein the effluent which is depleted in nitrate does not contain more than 0.3 g/l nitrate.

25. A process according to claim 9, wherein the effluent which is depleted in nitrate does not contain more than 0.5 g/l nitrate.

26. A process according to claim 12, wherein flocculation is conducted with a flocculating agent selected from the group consisting of alginates, xanthan gum, ferric chloride, aluminum sulfate, and polyacrylamide.

27. A process according to claim 9, wherein the effluents to be treated comprise suspended solid matter.

28. A process according to claim 1 wherein said agent supplying calcium is calcium aluminate and hydrated double-or mixed calcium nitroaluminate is added in a proportion of 10% to 50% by weight relative to the weight of said calcium aluminate to initiate the precipitation reaction.

29. A process according to claim 9, wherein manure is the material to be treated by the process and wherein the liquid effluent obtained in step (4) is clear, decolorized and deodorized.

30. A process according to claim 9, wherein the material to be treated by the process contains at least one undesirable cation and wherein the effluent obtained in step (4) contains a lower concentration of said at least one undesirable cation than the material to be treated.

31. A process according to claim 14, wherein the solution to be treated by the process is a water polluted with nitrates and wherein the purified water obtained in step (5) is clear, decolorized and deodorized.

32. A process according to claim 14, wherein the material to be treated by the process contains at least one undesirable cation and wherein the effluent obtained in step (5) contains a lower concentration of said at least one undesirable cation than the material to be treated.
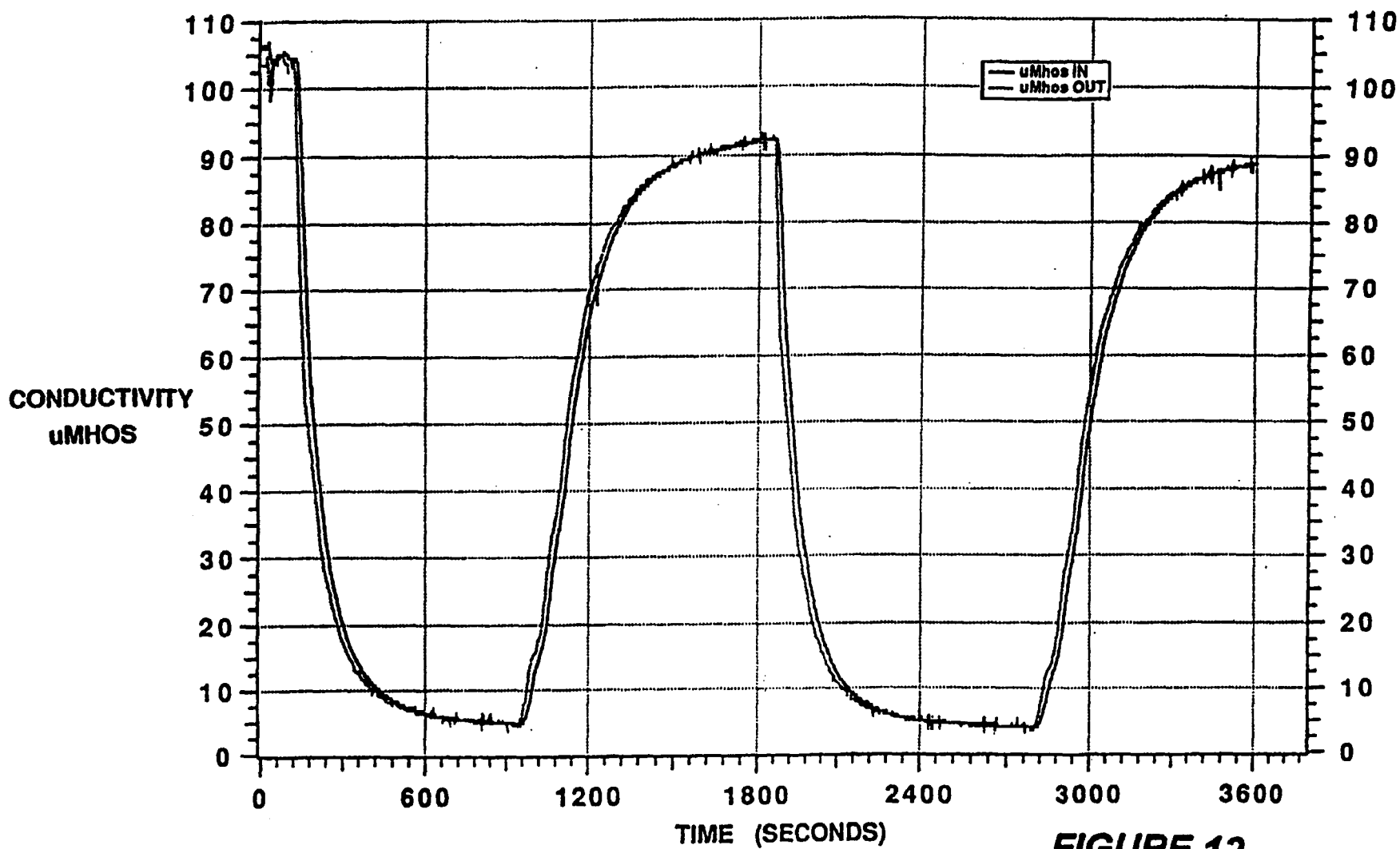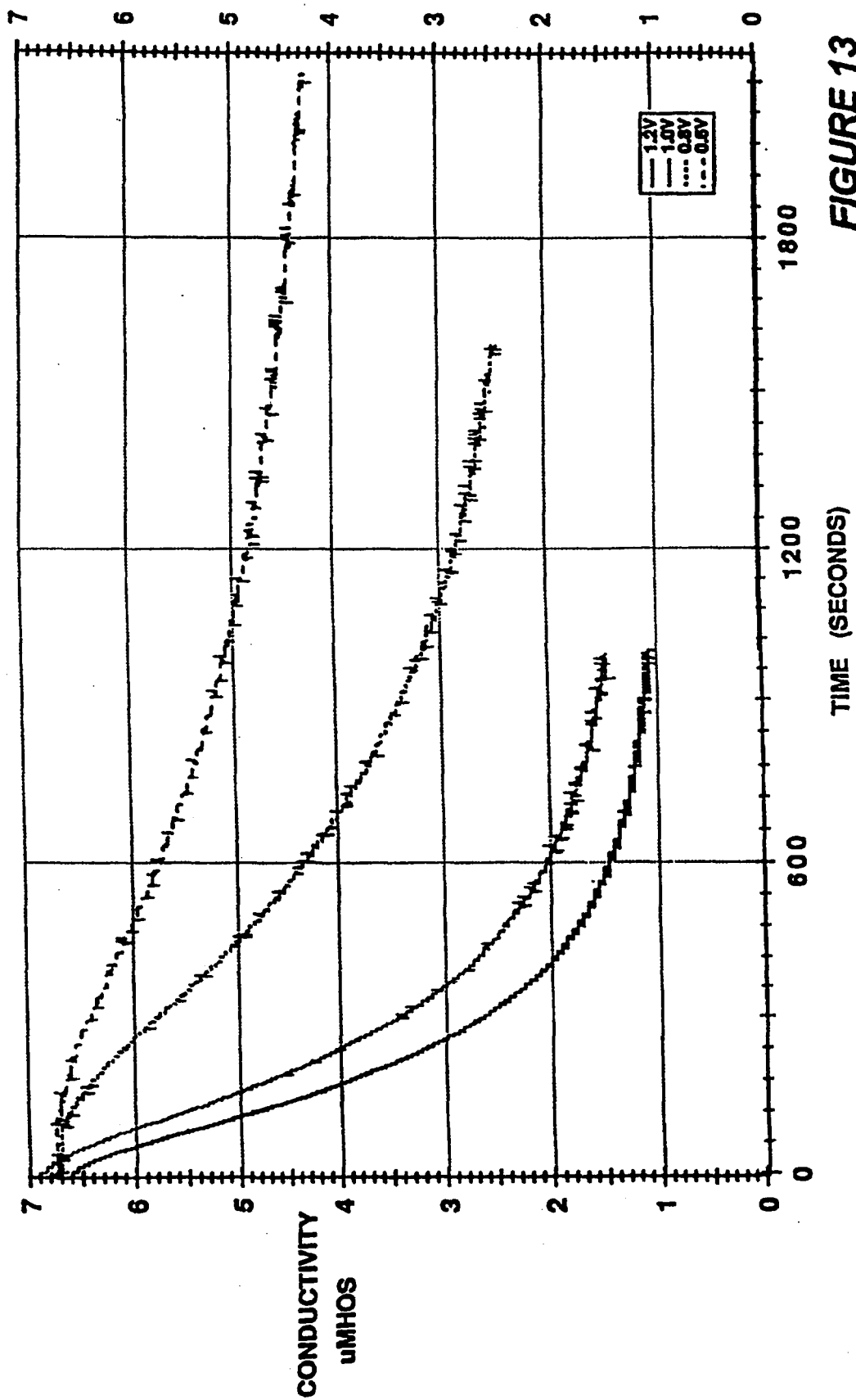
* * * * *

60

65

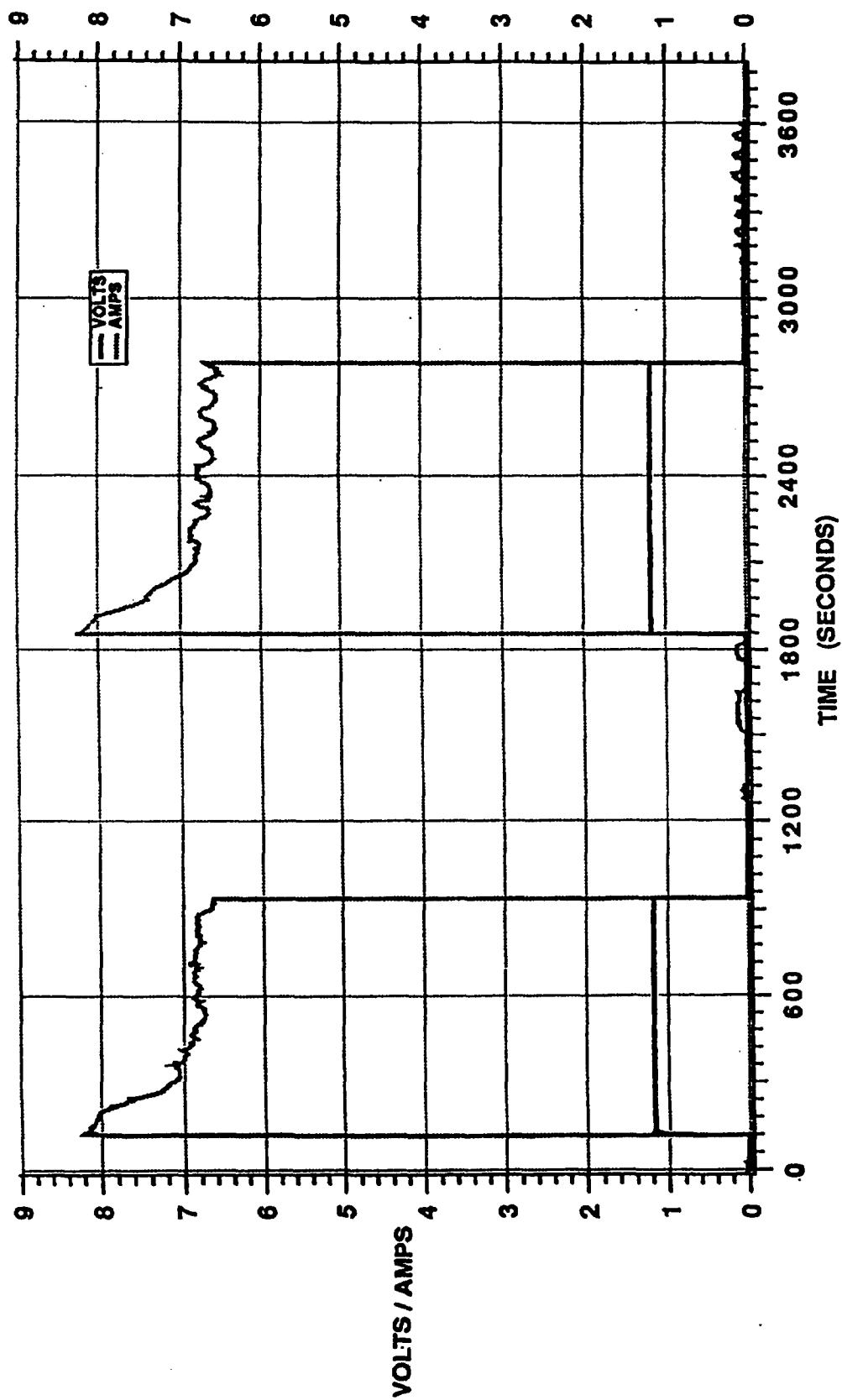**Method and Apparatus for Capacitive Deionization, Electrochemical Purification, and Regeneration of Electrodes**
Patent Number: 5,425,858
Date of Patent: June 20, 1995
Assignee: The Regents of the University of California, Oakland, California

United States Patent [19]

Farmer

[54] **METHOD AND APPARATUS FOR CAPACITIVE DEIONIZATION, ELECTROCHEMICAL PURIFICATION, AND REGENERATION OF ELECTRODES**

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[73] Assignee: **The Regents of the University of California**, Oakland, Calif.

[21] Appl. No.: **246,692**

[22] Filed: **May 20, 1994**

[51] Int. Cl.^{6} C02F 1/461
[52] U.S. Cl. 204/149; 204/164; 204/186; 204/267; 204/272; 204/302; 210/748
[58] Field of Search 204/149, 186, 267, 272, 204/164, 302; 210/748

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Primary Examiner—Kathryn Gorgos
Assistant Examiner—Arun S. Phasge
Attorney, Agent, or Firm—Henry P. Sartorio

[57] **ABSTRACT**

An electrochemical cell for capacitive deionization and electrochemical purification and regeneration of electrodes includes two oppositely disposed, spaced-apart end plates, one at each end of the cell. Two generally identical single-sided end electrodes, are arranged one at each end of the cell, adjacent to the end plates. An insulator layer is interposed between each end plate and the adjacent end electrode. Each end electrode includes a single sheet of conductive material having a high specific surface area and sorption capacity. In the preferred embodiment, the sheet of conductive material is formed of carbon aerogel composite. The cell further includes a plurality of generally identical double-sided intermediate electrodes that are equidistally separated from each other, between the two end electrodes. As the electrolyte enters the cell, it flows through a continuous open serpentine channel defined by the electrodes, substantially parallel to the surfaces of the electrodes. By polarizing the cell, ions are removed from the electrolyte and are held in the electric double layers formed at the carbon aerogel surfaces of the electrodes. As the cell is saturated with the removed ions, the cell is regenerated electrically, thus significantly minimizing secondary wastes.

37 Claims, 16 Drawing Sheets

RAW WATER

10

STACK

12

─   +

STACK

(X)

23   25

WASTE   PRODUCT

PRIOR ART

FIGURE 1

12

14

18

21

20

16
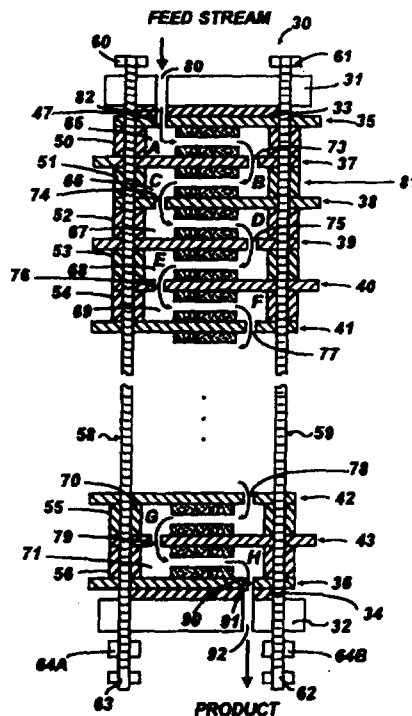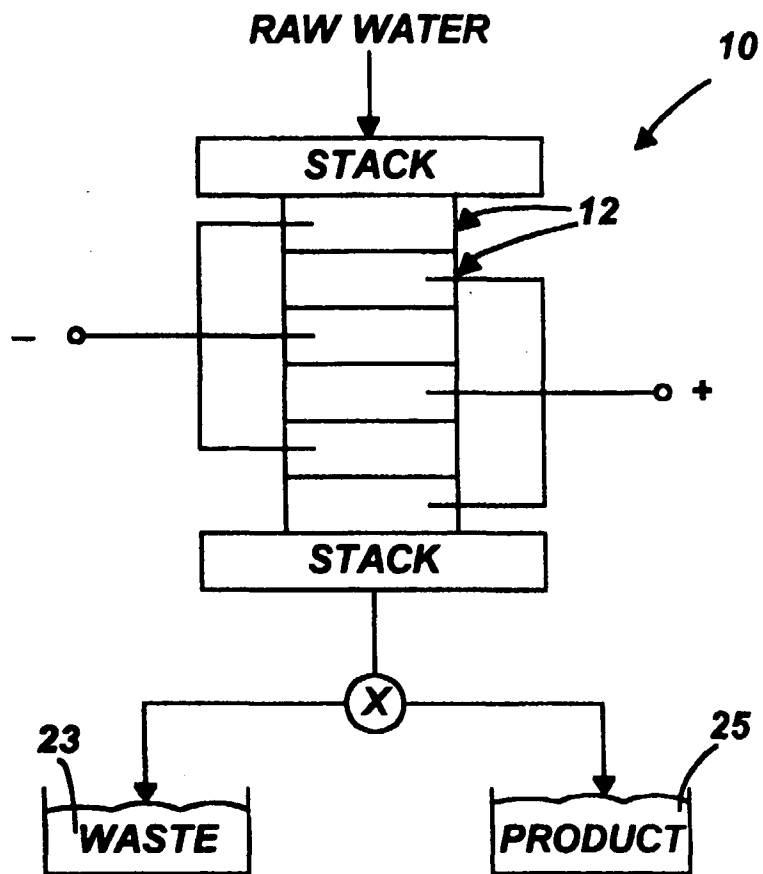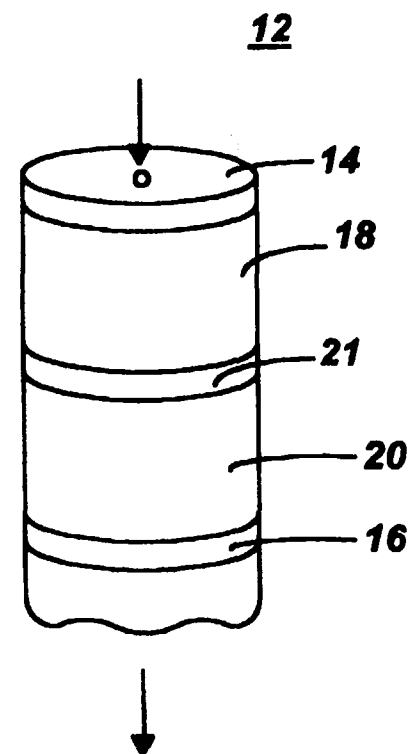
PRIOR ART

FIGURE 2

FEED STREAM   *30*
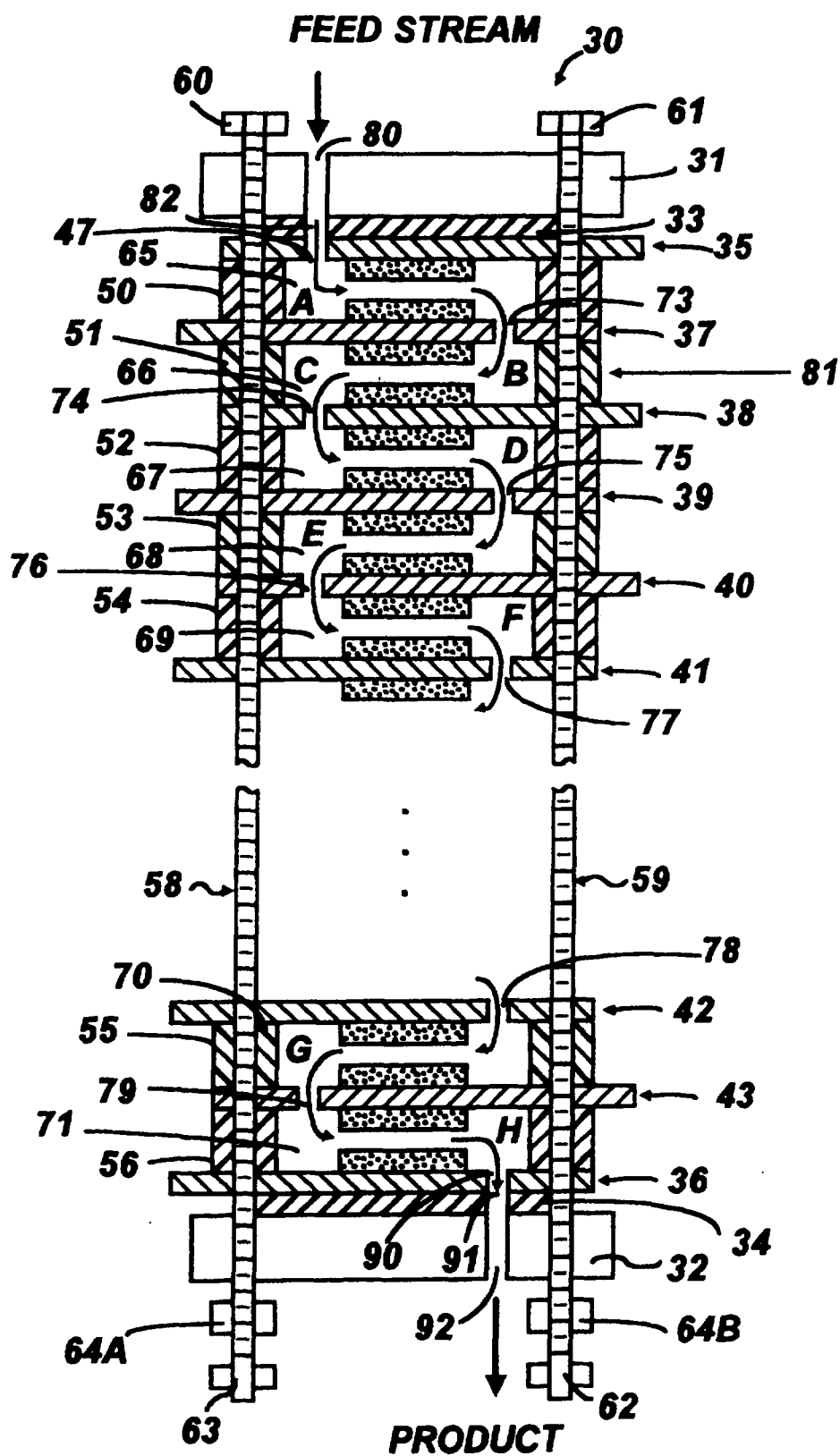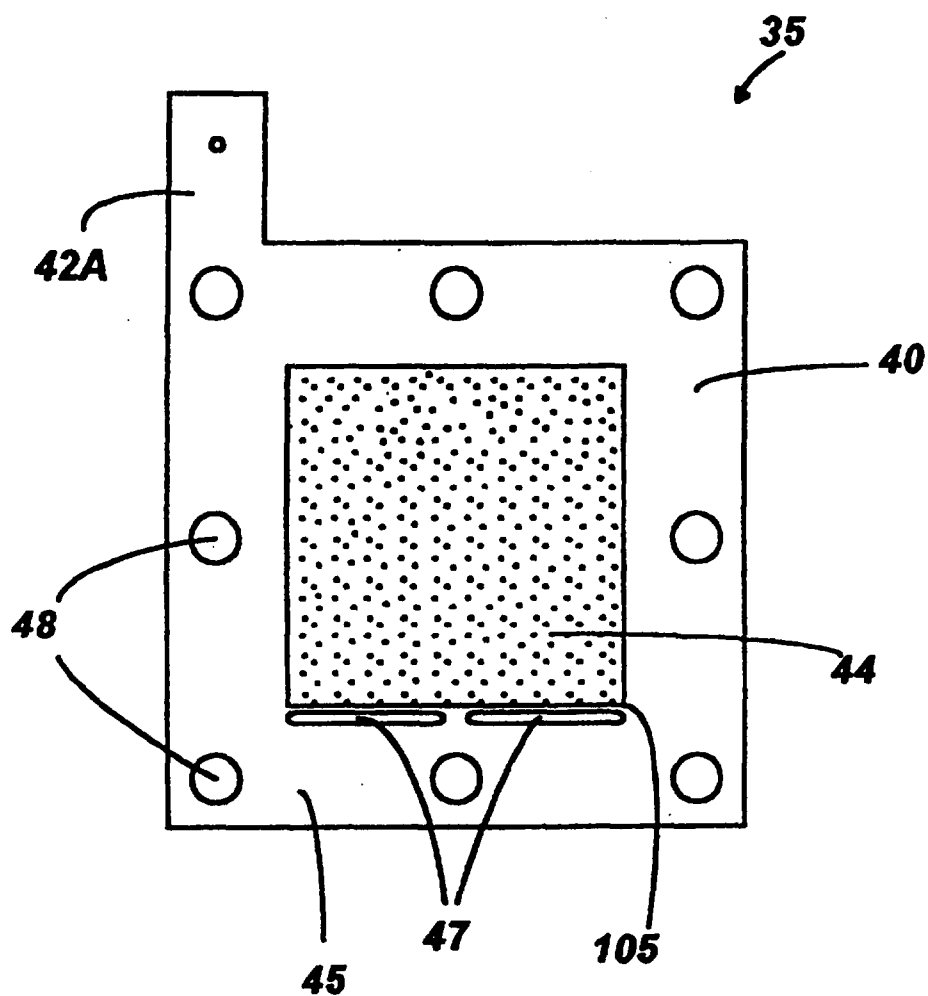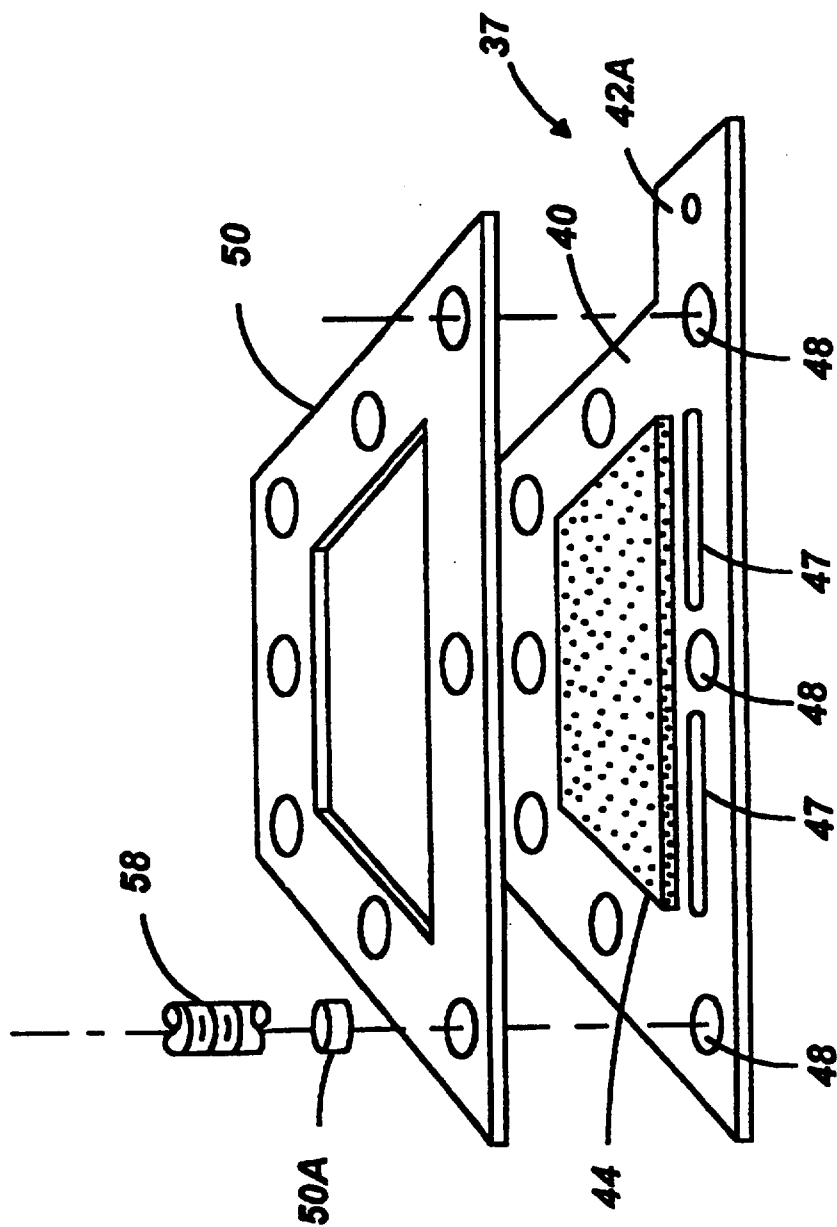
FIGURE 3

FIGURE 4A

FIGURE 4B

FIGURE 5

FIGURE 6

175

REGEN.
TANK

REGEN.
TANK

179

30A

181b

CELL
A

181a

181c

176

POWER
SUPPLY &
SWITCHING

180b 180c

30B

CELL
B

180a

182

178

CONTROLLER

185

188

SENSORS

DISCHARGE

COMPUTER

190

A/D
CONVERTER

SENSORS

187

DISCHARGE

RAW FLUID STREAM

152

FIGURE 7

PURIFIED FLUID
STREAM
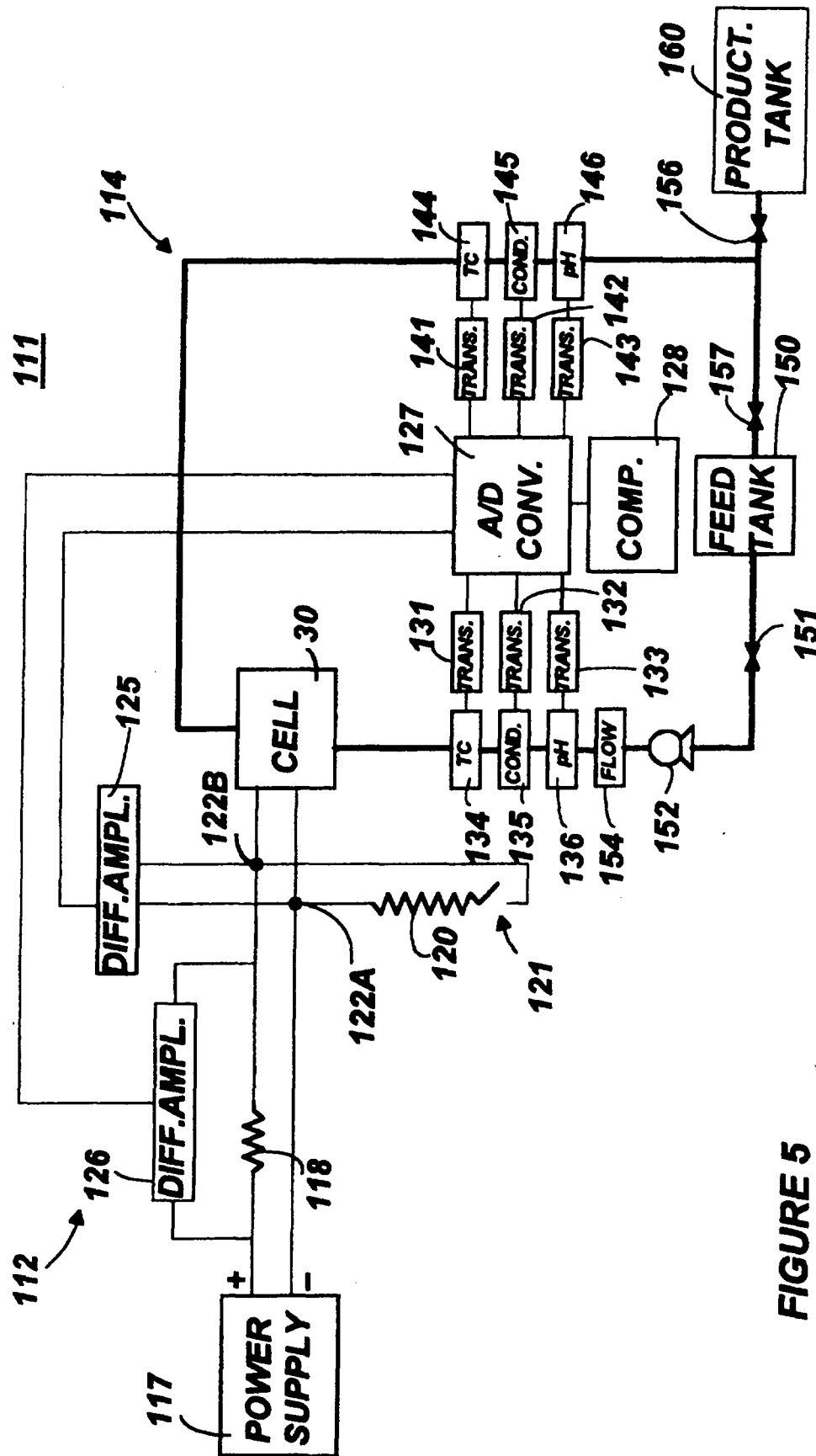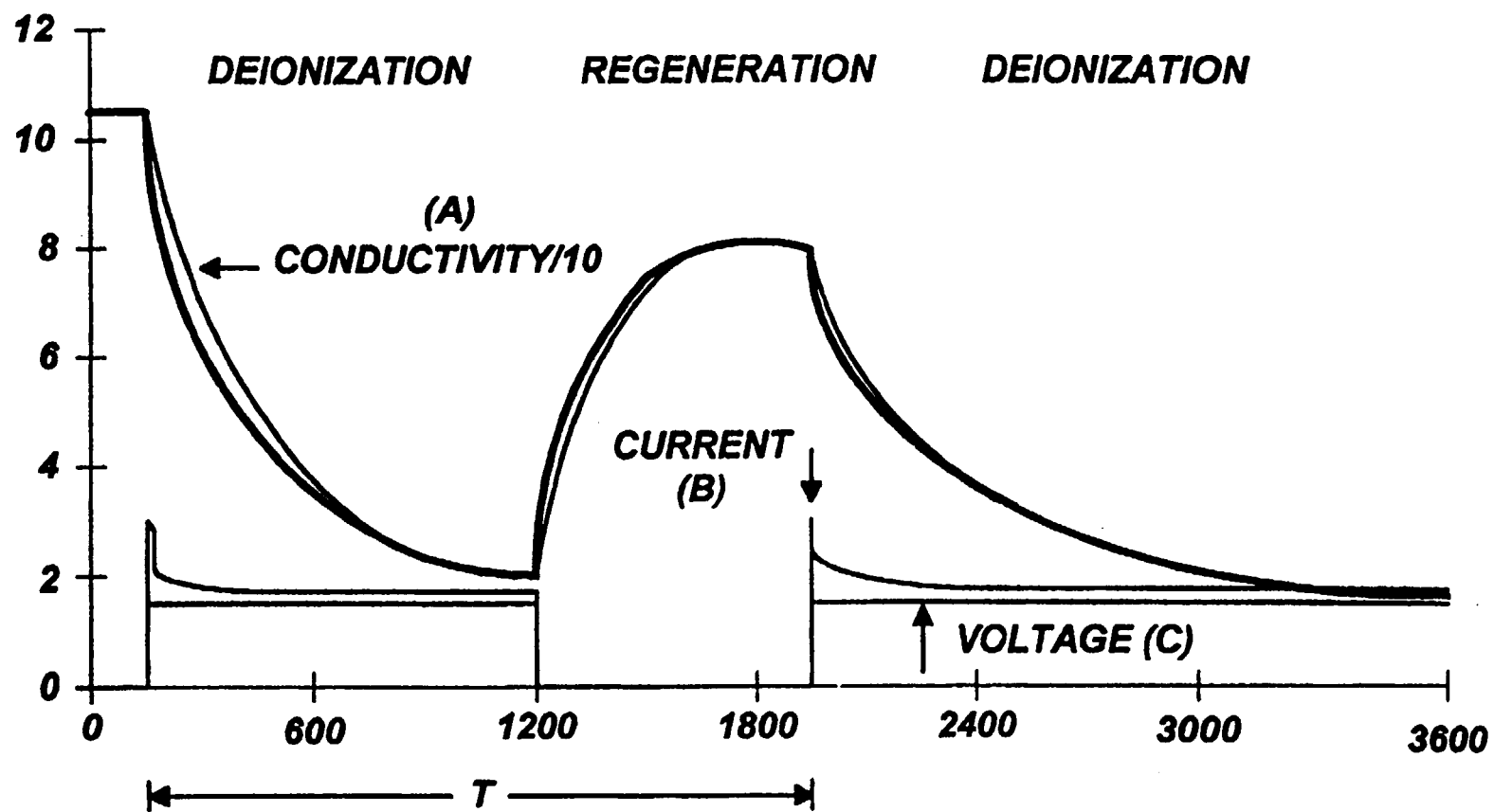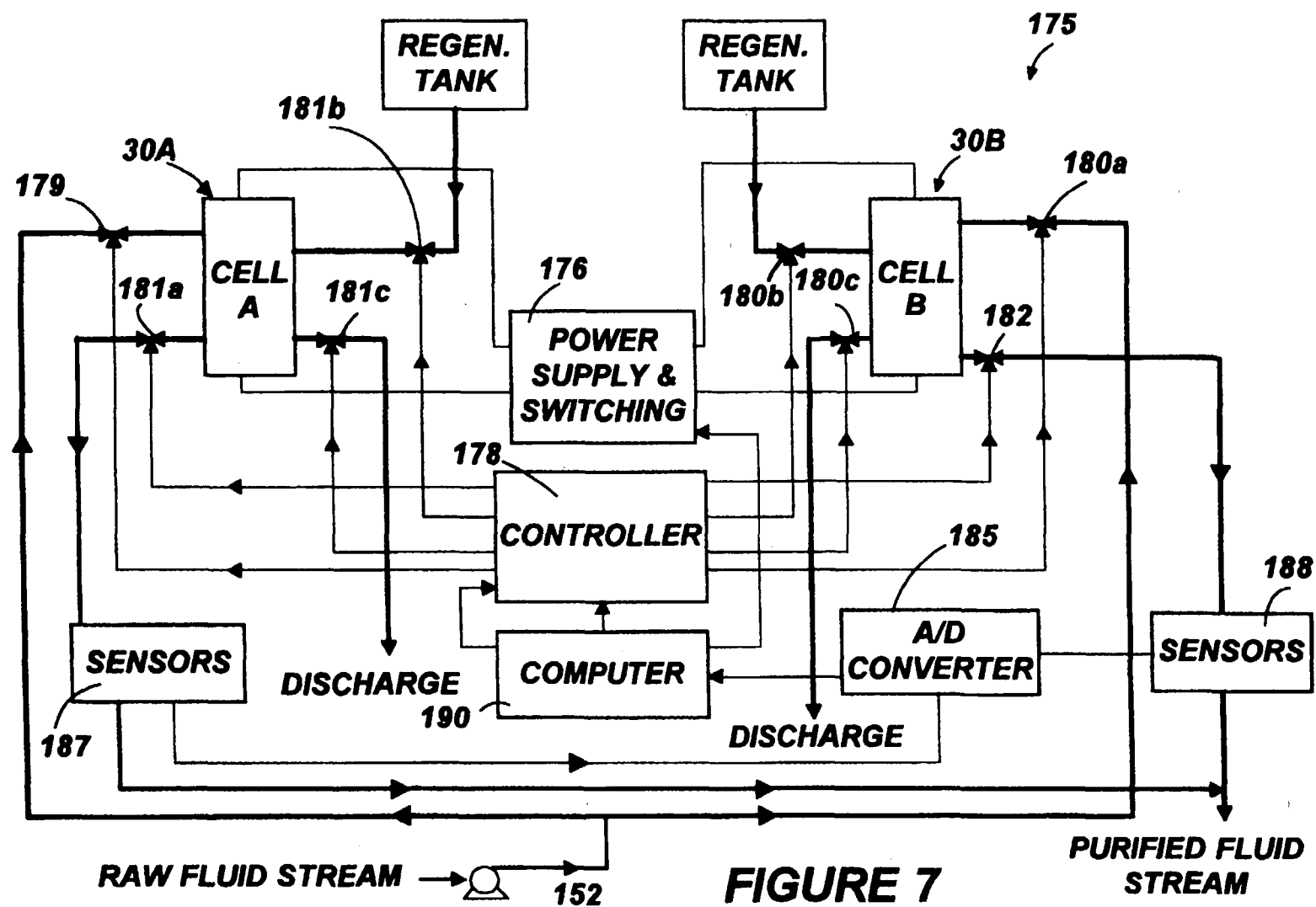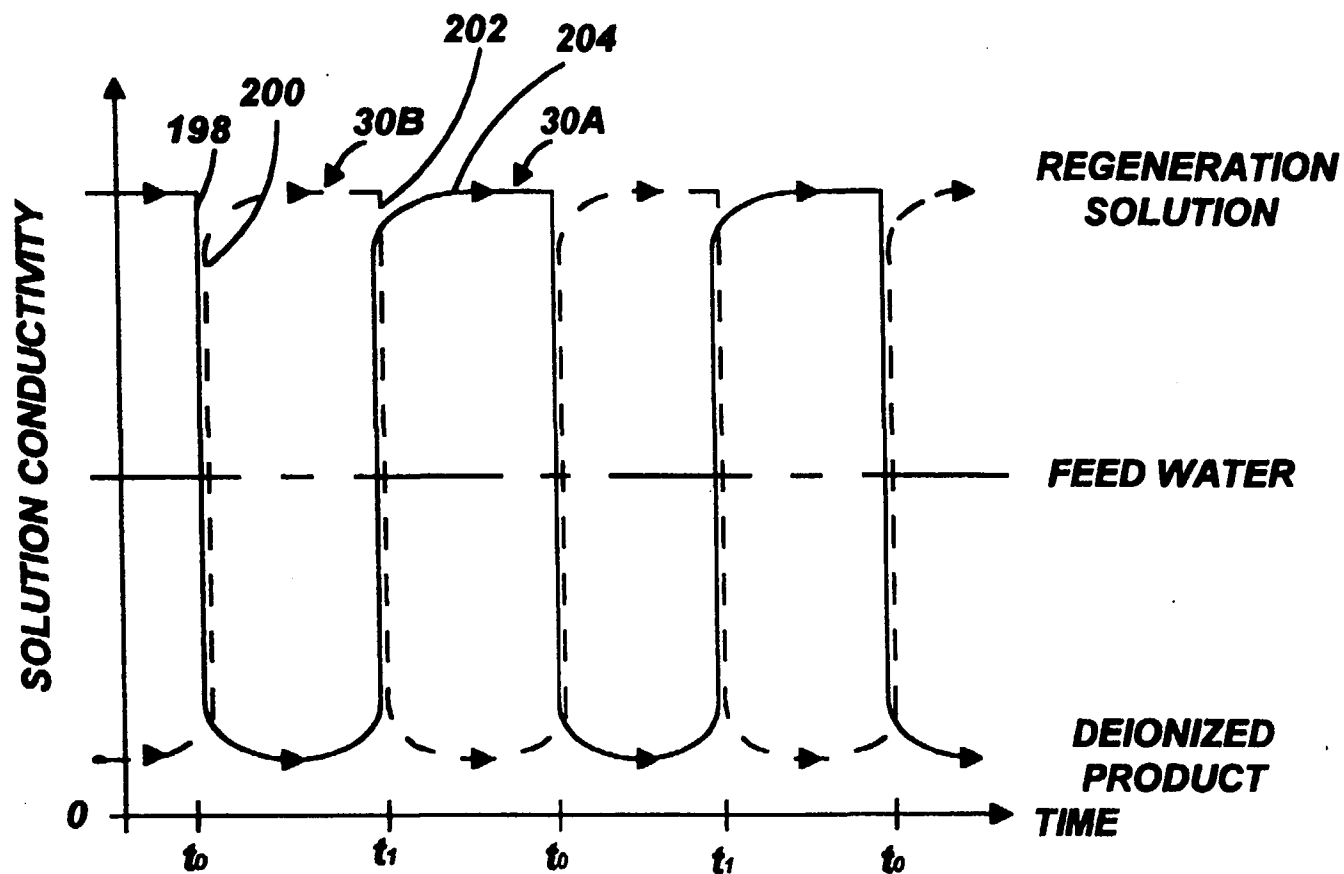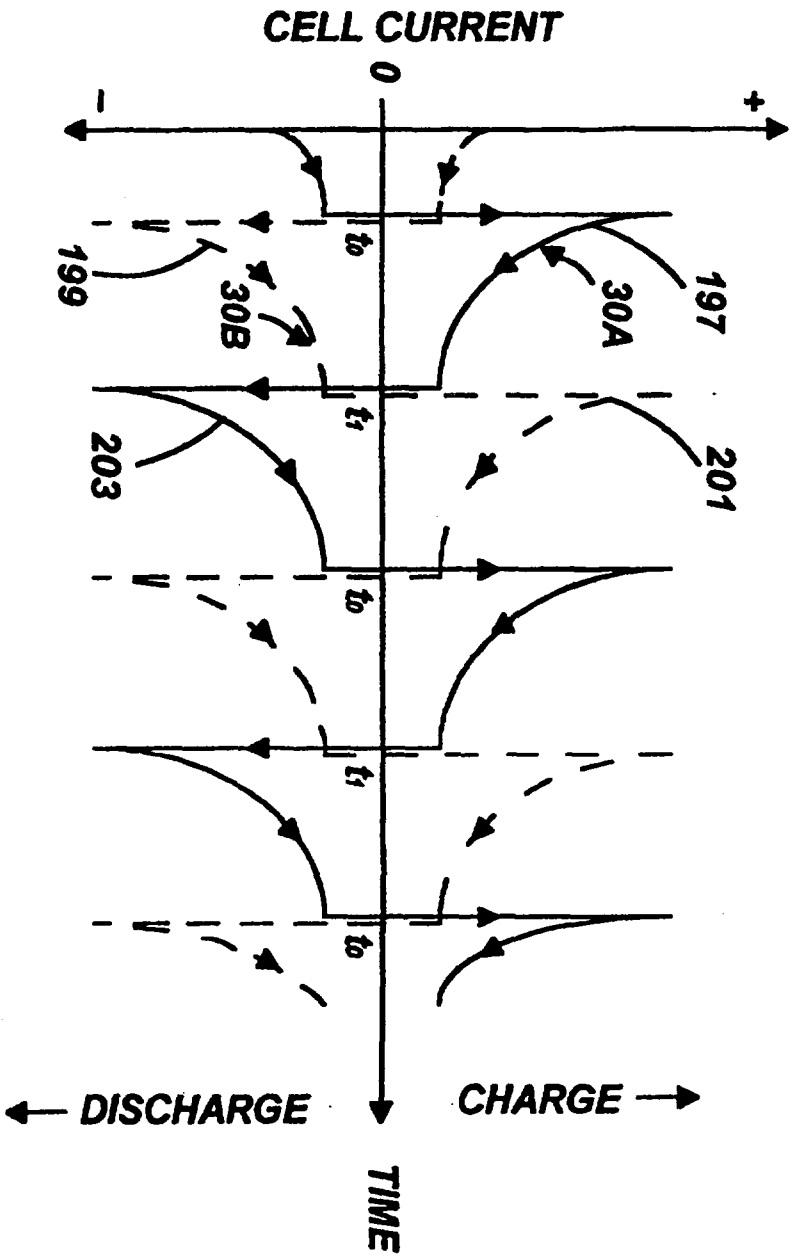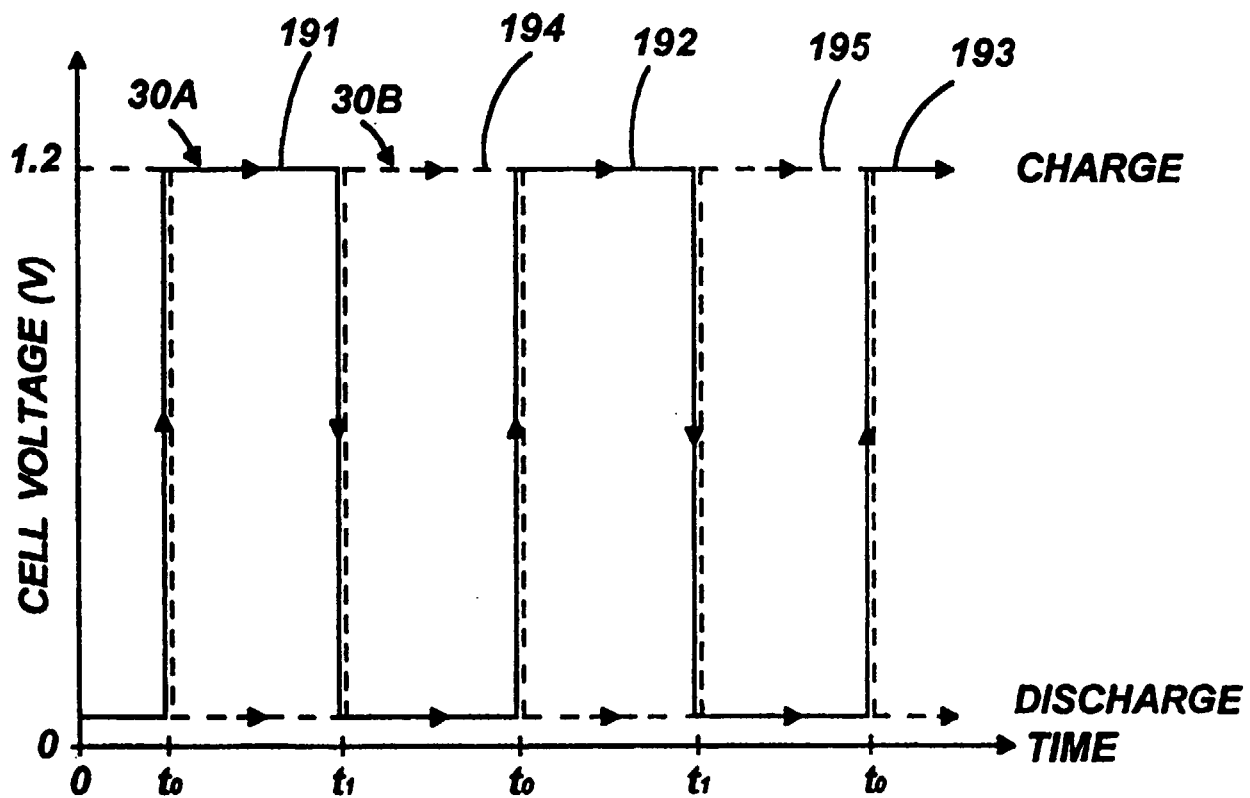
FIGURE 8A

FIGURE 8B

FIGURE 8C

FIGURE 9

FIGURE 10

INFLOW

250

252

253

255

254

FIGURE 11B

252

OUTFLOW
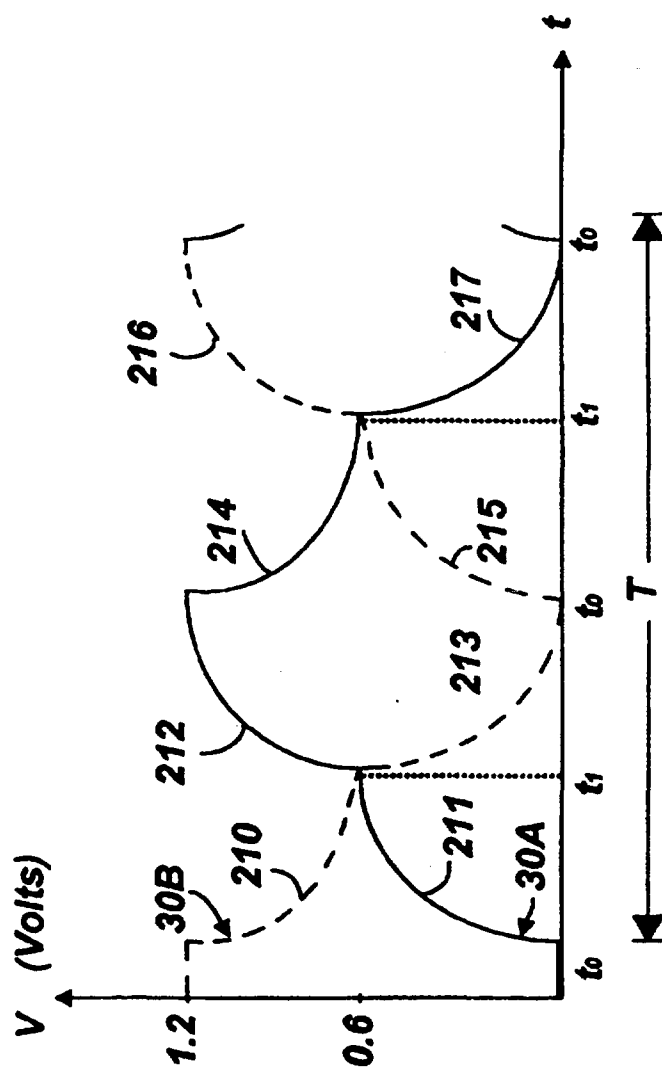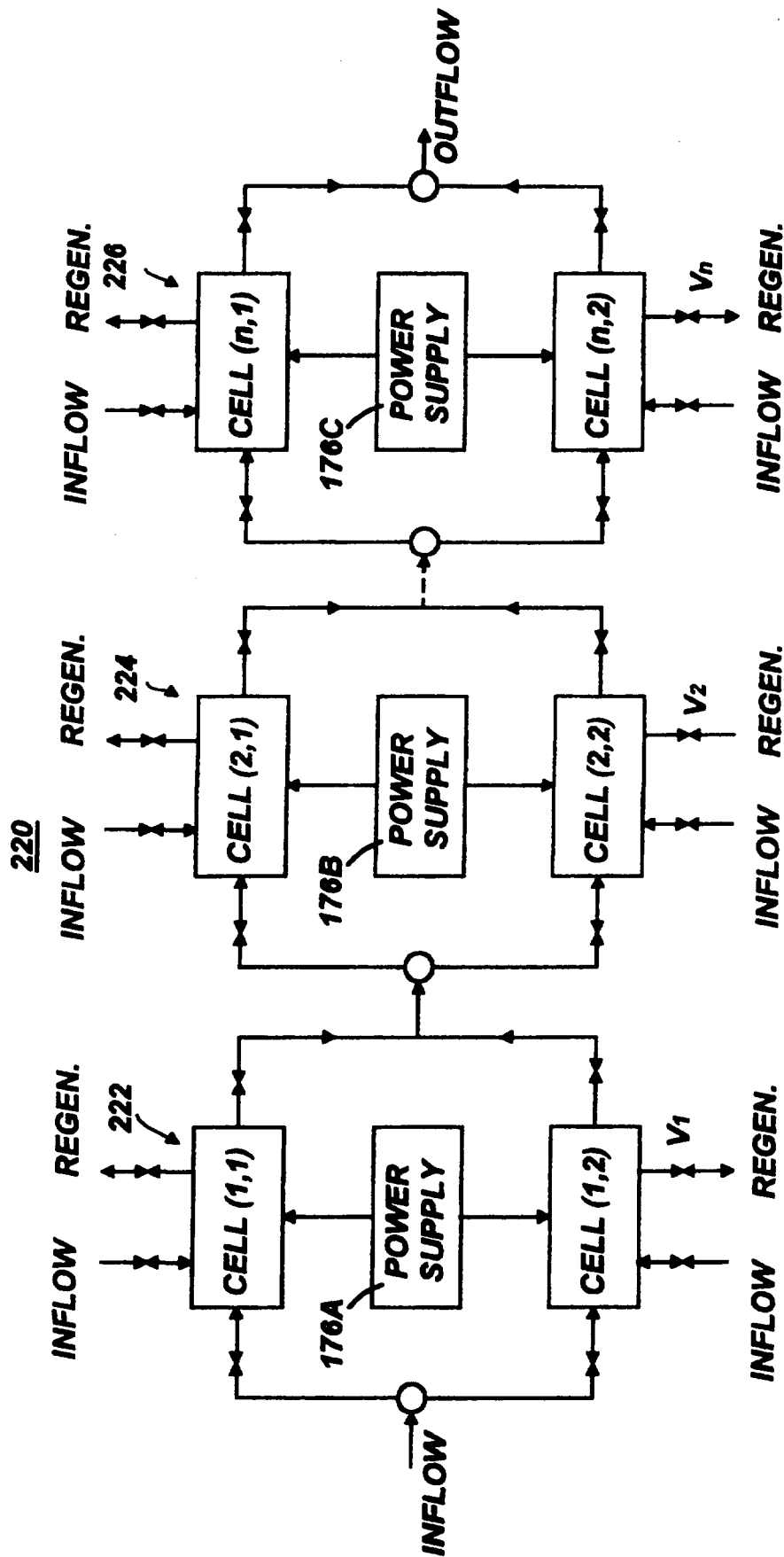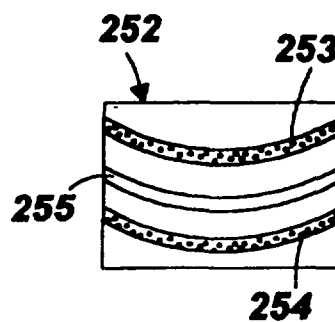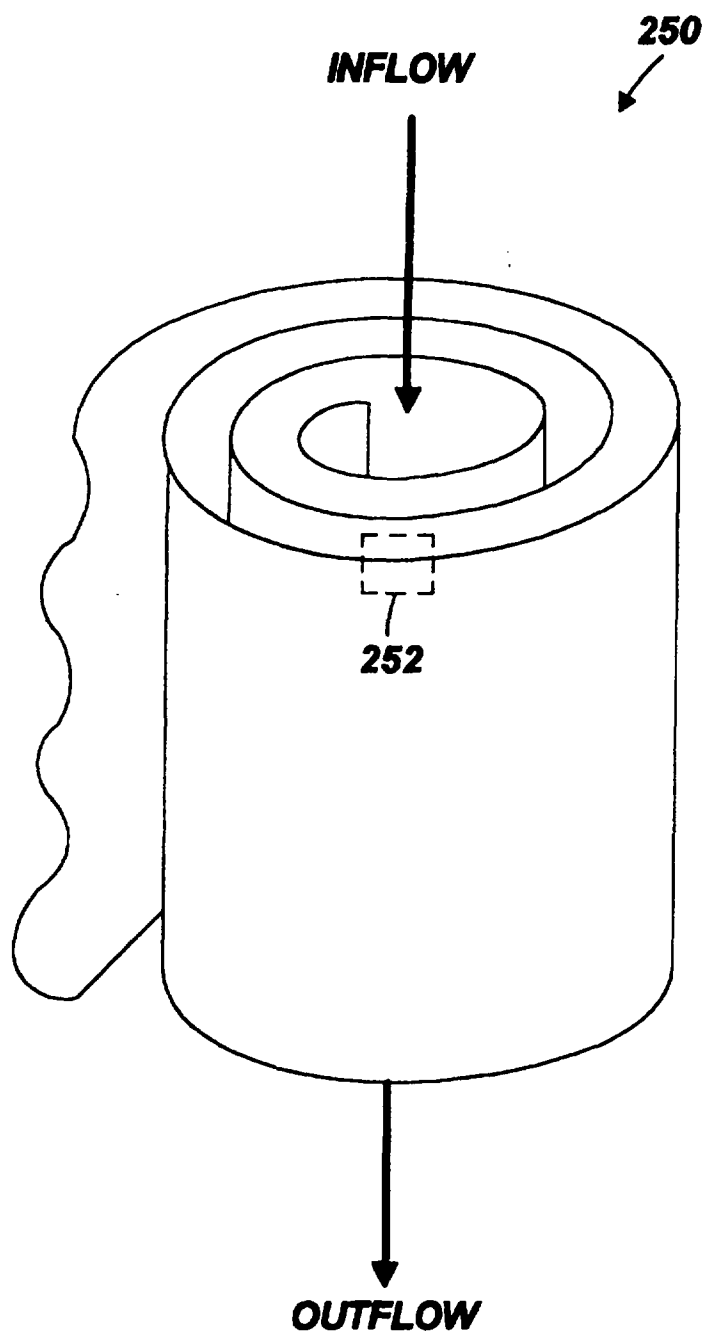
FIGURE 11A

FIGURE 12

FIGURE 13

FIGURE 14

METHOD AND APPARATUS FOR CAPACITIVE DEIONIZATION, ELECTROCHEMICAL PURIFICATION, AND REGENERATION OF ELECTRODES

STATEMENT OF GOVERNMENT RIGHTS

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is generally directed to the field of electrochemistry, and it more specifically relates to a new separation method and apparatus for removing ions, contaminants and impurities from water and other aqueous process streams, and for placing the removed ions back into solution during regeneration of the apparatus.

2. Background Art

The separation of ions and impurities from electrolytes has heretofore been generally achieved using a variety of conventional processes including: ion exchange, reverse osmosis, electrodialysis, electrodeposition, or filtering. Several other methods have been proposed and address the problems associated with the conventional separation processes. However, these proposed methods have not been completely satisfactory for specific applications nor useful for all applications, and have not met with universal commercial success or complete acceptance. One such proposed ion separation method, which relates to a process for desalting water based on periodic sorption and desorption of ions on the extensive surface of porous carbon electrodes, will be described later in more detail.

The conventional ion exchange process has been used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and waste water in various industries. This process generates large volumes of corrosive secondary wastes that must be · treated for disposal through regeneration processes. Existing regeneration processes are typically carried out following the saturation of the columns by ions, by pumping regeneration solutions, such as concentrated acids, bases, or salt solutions through the columns. These routine maintenance measures produce significant secondary wastes, as well as periodic interruptions of the deionization process.

Secondary wastes resulting from the regeneration of the ion exchangers typically include used anion and cation exchange resins, as well as contaminated acids, bases and/or salt solutions. For example, H_2SO_4 solutions have been used for the regeneration of cation columns in metal finishing and power industries; and HNO_3 solutions have been used for the regeneration of cation columns used in processing nuclear materials.

In some instances, the secondary radioactive wastes are extremely hazardous and can cause serious environmental concerns. For instance, during plutonium processing, resins and solutions of HNO_3 become contaminated with PuO_2^{++} and other radioisotopes. In this case, every pound of cation exchange resin requires approximately 100 pounds of 10 wt. % HNO_3 and 2 to 3 pounds of rinse water for regeneration. Similarly, every pound of anion exchange resin requires approxi-

mately 100 pounds of 10 wt. % NaOH and 2 to 3 pounds of rinse water for regeneration. Given the high and increasing cost of disposal of secondary wastes in mined geological repositories, there is tremendous and still unfulfilled need for reducing, and in certain applications, eliminating the volume of secondary wastes.

Another example is the use of the ion exchange process for industrial purposes, such as in the electroplating and metal finishing industries. A typical electroplating process includes immersing the article to be electroplated in an electroplating bath which contains dissolved metals, such as nickel, cadmium zinc, copper, silver and/or gold, as well as a variety of salts, and then rinsing this article. Once the electroplating process is completed, the plated article is rinsed to remove residual plating solution and associated contaminants. The rinsing process includes hanging the article on a rack above a rinse tank and spraying it with rinse water from spray nozzles around the top of the rinse tank.

The rinse water becomes contaminated, and a major dilemma currently facing the industry relates to the difficulties, cost considerations and the environmental consequences for disposing of the contaminated rinse solution. A typical treatment method for the contaminated rinse water is the ion exchange process.

Other exemplary processes which further illustrate the problems associated with ion exchange include residential water softening and the treatment of boiler water for nuclear and fossil-fueled power plants. At the present time, domestic water softeners use a concentration solution of sodium chloride to regenerate a bed of ion exchange resin. Unfortunately, such water softeners result in a relatively high concentrated solution of sodium chloride in the drinking water produced by the system. Therefore, additional desalination devices, such as reverse osmosis filters are needed to remove the excess sodium chloride introduced during regeneration. It should be noted that people on low-salt diets also require low-salt water. A solution that contains contaminants from the ion exchange resin is produced during regeneration and must be discharged to the sewer.

Boiler water for nuclear and fossil-fueled power plants is treated with ion exchange to remove ionic contaminants such as Mg^{++}, Ca^{++}, Cu^{++}, and Cl^-, and is essential for the prevention of pitting, stress corrosion cracking, and scaling of heat transfer surfaces. Such treatment is particularly important on nuclear powered ships and submarines. Another important example is the production of high-purity water for semiconductor processing. Other applications could include the removal of toxic ions, especially those containing selenium, from waters produced by agricultural irrigation.

Therefore, there is still a significant and growing need for a new method and apparatus for deionization and subsequent regeneration, which significantly reduce, if not entirely eliminate secondary wastes in certain applications. This method and apparatus should not require salt additions for ion regeneration in a water softening system, and further should not require additional desalination devices, such as reverse osmosis filters, to remove the excess sodium chloride introduced during regeneration.

Additionally, the new method and apparatus should enable the separation of any inorganic or organic ion or dipole from any ionically conducting solvent, which could be water, an organic solvent, or an inorganic

3

solvent. For example, it should be possible to use such a process to purify organic solvents, such as propylene carbonate, for use in lithium batteries and other energy storage devices. Furthermore, it should be possible to use such a process to remove organic ions, such as for- 5 mate or acetate from aqueous streams.

The new method and apparatus should further be adaptable for use in various applications, including without limitation, treatment of boiler water in nuclear and fossil power plants, production of high-purity water 10 for semiconductor processing, removal of toxic and hazardous ions from water for agricultural irrigation, and desalination of sea water.

In the conventional reverse osmosis systems, water is forced through a membrane, which acts as filter for 15 separating the ions and impurities from electrolytes. Reverse osmosis systems require significant energy to move the water through the membrane. The flux of water through the membrane results in a considerable pressure drop across the membrane. This pressure drop 20 is responsible for most of the energy consumption by the process. The membrane will also degrade with time, requiring the system to be shut down for costly and troublesome maintenance.

Therefore, there is a need for a new method and 25 apparatus for deionization and ion regeneration, which substitute for the reverse osmosis systems, which do not result in a considerable pressure drop, which do not require significant energy expenditure, or interruption of service for replacing the membrane(s). 30

The conventional ion separation method relating to a process for desalting water based on periodic sorption and desorption of ions on the extensive surface of porous carbon electrodes is described in the Office of Saline Water Research and Development Progress Re- 35 port No. 516, March 1970, U.S. Department of the Interior PB 200 056, entitled *The Electrosorb Process for Desalting Water*, by Allan M. Johnson et al., hereinafter referred to as the "Department of the Interior Report" and further in an article entitled "*Desalting by Means of* 40 *Porous Carbon Electrodes*" by J. Newman et al., in J. Electrochem. Soc.: Electrochemical Technology, March 1971, Pages 510–517, hereinafter referred to as the "Newman Article", both of which are incorporated herein by reference. A comparable process is also de- 45 scribed in NTIS research and development progress report No. OSW-PR-188, by Danny D. Caudle et al., *Electrochemical Demineralization of Water with Carbon Electrodes*, May, 1966.

The Department of the Interior Report and the New- 50 man Article review the results of an investigation of electrosorption phenomena for desalting with activated carbon electrodes, and discuss the theory of potential modulated ion sorption in terms of a capacitance model. This model desalination system 10 is diagrammatically 55 illustrated in FIG. 1, and includes a stack of alternating anodes and cathodes which are further shown in FIG. 2, and which are formed from beds of carbon powder or particles in contact with electrically conducting screens (or sieves). Each cell 12 includes a plurality of anode 60 screens 14 interleaved with a plurality of cathode screens 16, such that each anode screen 14 is separated from the adjacent cathode screen 16 by a first and second beds 18, 20, respectively of pretreated carbon powder. These two carbon powder beds 18 and 20 are sepa- 65 rated by a separator 21, and form the anode and cathode of the cell 12. In operation, and as shown in FIG. 1, raw water is flown along the axial direction of the cells 12,

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perpendicularly to the surface of the electrode screens 14, 16, to be separated by the system 10 into waste 23 and product 25.

However, this model system 10 suffers from several disadvantages, among which are the following:

1. The carbon powder beds 18 and 20 are used as electrodes and are not "immobilized". The primary carbon particles and fines, smaller particles generated by erosion of the primary particles, can become readily entrained in the flow, which eventually depletes the carbon bed, reduces the efficiency of the deionization or desalination system 10, and necessitates maintenance.
2. It is significant that raw water must flow axially through these electrode screens 14 and 16, beds of carbon powder 18 and 20, and separators 21, which cause significant pressure drop and large energy consumption.
3. The carbon bed electrodes 18 and 20 are quite thick, and a large potential drop is developed across them, which translates into lower removal efficiency and higher energy consumption during operation.
4. Even though the carbon particles "touch", i.e., adjacent particles are in contact with each other, they are not intimately and entirely electrically connected. Therefore, a substantial electrical resistance is developed, and significantly contributes to the process inefficiency. Energy is wasted and the electrode surface area is not utilized·effectively.
5. The carbon beds 18 and 20 have a relatively low specific surface area.
6. The carbon powder bed electrodes 18 and 20 degrade rapidly with cycling, thus requiring continuous maintenance and skilled supervision.
7. The model system 10 is designed for one particular application, namely sea water desalination, and does not seem to be adaptable for use in other applications.

Therefore, there is still a significant unfulfilled need for a new method and apparatus for deionization and regeneration, which, in addition to the ability to significantly reduce if not to completely eliminate secondary wastes associated with the regeneration of ion exchange columns, do not result in a considerable pressure drop of the flowing process stream, and do not require significant energy expenditure. Furthermore, each electrode used in this apparatus should be made of a structurally stable, porous, monolithic solid. Such monolithic electrodes should not become readily entrained in, or depleted by the stream of fluid to be processed, and should not degrade rapidly with cycling. These electrodes should have a very high specific surface area; they should be relatively thin, require minimal operation energy, and have a high removal efficiency. The new method and apparatus should be highly efficient, and should be adaptable for use in a variety of applications, including, but not limited to sea water desalination.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a new separation process and apparatus for removing ions, contaminants, impurities and like matters from water and other aqueous process streams, and for subsequently electrically placing the removed ions back into a solution during the regeneration process.

It is another object of the present invention to provide a new separation process and apparatus which

address the concerns associated with conventional separation devices, and which provide adequate solutions thereto.

It is yet another object of the present invention to provide a new separation process and apparatus which capacitively deionize streams of electrolyte, and which regenerate the apparatus electrically.

It is still another object of the present invention to provide a new separation process and apparatus which do not utilize chemical regeneration processes, and thus significantly reduce, and in certain application completely eliminate secondary wastes associated with the operation of ion exchange resins.

It is another object of the present invention to provide a new separation process and apparatus which do not result in a considerable pressure drop of the electrolyte.

It is still another object of the present invention to provide a new separation process and apparatus that are more energy efficient than conventional processes.

It is a further object of the present invention to provide a new separation apparatus comprising electrodes which do not become readily entrained in, or depleted by the electrolyte, and which do not degrade rapidly with cycling.

It is yet another object of the present invention to provide a new separation apparatus comprising electrodes which have a significantly high specific surface area and a high removal efficiency, which are relatively thin, and which require minimal operation energy.

It is still another object of the present invention to provide a new separation process and apparatus which are highly efficient and adaptable for use in a variety of applications, including, but not limited to domestic water softening, industrial water softening, waste water purification, and sea water desalination.

It is a further object of the present invention to provide a new separation process and apparatus which do not require salt additions for ion regeneration in a water softening system, and which further do not require additional desalination devices, such as reverse osmosis filters to remove the excess sodium chloride introduced during regeneration.

It is yet another object of the present invention to provide a new separation process which is chemically stable, thus preventing the novel apparatus from prematurely degrading.

It is still another object of the present invention to provide a new separation process and system with continuous deionization and regeneration capability.

It is yet another object of the present invention to provide a new separation method and system with selective and progressive deionization and regeneration capability.

In the preferred embodiment, the new separation process is used for the deionization of water and the treatment of aqueous wastes. This new process will also be referred to as capacitive deionization. Unlike the conventional ion exchange processes, no chemicals, whether acids, bases, or salt solutions, are required for the regeneration of the system; instead, electricity is used.

A stream of electrolyte to be processed, which contains various anions and cations, electric dipoles, and/or suspended particles is passed through a stack of electrochemical capacitive deionization cells. Each of these cells includes numerous carbon aerogel electrodes having exceptionally high specific surface areas (for example, 400–1000 m^2/gm). By polarizing the cell, non-reducible and non-oxidizable ions are removed from the fluid stream electrostatically and held in the electric double layers formed at the surfaces of the electrodes. Some metal cations are removed by electrodeposition. Electric dipoles also migrate to and are trapped at the electrodes. Small suspended particles are removed by electrophoresis. Therefore, the fluid stream leaving the cell is purified.

In conventional desalting and purification processes, such as evaporation and reverse osmosis, energy is expanded removing water from salt and other impurities. Consequently, the required energy is great. According to the present inventive capacitive deionization process, energy is expanded using electrostatics to remove salt and other impurities from the fluid, and, as a result, is orders-of-magnitude more energy efficient than conventional processes. Furthermore, the pressure drop in the capacitive deionization cells is dictated by channel flow between parallel surfaces of monolithic, microporous solids (i.e., the electrodes), hence, it is insignificant compared to that needed to force water through the permeable membrane required by the reverse osmosis process.

One of the features of the inventive separation system is that no expensive ion exchange membranes are required for the separation of the electrodes. All the anodes and cathodes of the electrode pairs are connected in parallel. The present system is modular, and can be readily expanded to include 96 electrode pairs (192 electrodes) with a total anode or cathode surface area of approximately 2.7×10^8 cm^2. Ultimately, the system capacity can be increased to any desired level by expanding the cell(s) to include a greater number of electrode pairs. The conductivity and the pH of the inlet and exit streams are continuously monitored.

Initial experiments have been conducted with complete recycle (batch mode), or with no recycle (continuous mode). In some of these experiments, sodium chloride solution was used. The conductivity of this solution was comparable to hard tap water and was reduced to less than 85 percent of its initial level by capacitive deionization. Greater separation is possible. In the continuous mode of operation, which was possible before saturation of the stack, it was possible to remove over 97% of the salt from water with an initial conductivity greater than 100 micromhos. With sufficient electrode capacity, the same or greater removal is possible at much higher ion concentrations.

Some advantages of the present invention include, but are not limited to the following:

1. Unlike the conventional osmosis process where water is forced through a membrane by pressure gradient, and unlike the conventional ion exchange process and the process described in the Newman Article and the Department of Interior Report, where fluid is flown through a packed bed, the present separation methods and systems do not require the electrolyte to flow through any porous media such as membranes or packed beds. In the present system, electrolyte flows in open channels formed between two adjacent, planar electrodes, which are geometrically parallel. Consequently, the pressure drop is much lower than conventional processes. The fluid flow can be gravity fed through these open channels, or alternatively, a pump can be used.

2. The present system does not require membranes, which are both troublesome and expensive, which rupture if overpressured, which add to the internal resistance of the capacitive cell, and which further reduce the system energy efficiency. This feature represents a significant advantage over the conventional reverse osmosis systems which include water permeable cellulose acetate membranes, and over the electrodialysis systems which require expensive and exotic ion exchange membranes.

3. The electrodes in the present system are composed of immobilized sorption media, such as monolithic carbon aerogel which is not subject to entrainment in the flowing fluid stream. Thus, material degradation due to entrainment and erosion is considerably less than in conventional packed carbon columns. This feature represents yet another significant advantage over the systems described in the Department of the Interior Report and the Newman Article where activated carbon is lost from the bed over the conventional ion exchange systems where ion exchange resin is lost from the beds.

4. The present systems and methods are inherently and greatly energy efficient. For instance, in both evaporation and reverse osmosis processes, water is removed from salt, while in the present systems, salt is removed from water, thus expending less energy.

5. The present systems and methods present superior potential distribution in the thin sheets of carbon aerogel. Unlike the deep, packed carbon beds used in the electrosorb process discussed in the Department of Interior Report and in the Newman Article, most of the carbon aerogel is maintained at a potential where electrosorption is very efficient. In deep, packed carbon beds, the potential drops to levels where the electrosorption process is not very effective. Furthermore, the specific surface area of the sorption media used in the present process is significantly greater than that of carbon powder. This feature also contributes significantly to overall process efficiency.

Additionally, the present separation processes and systems have several important applications, among which are the following:

1. Removal of various ions from waste water without the generation of acid, base, or other similar secondary wastes. This application may be especially important in cases involving radionuclides, where the inventive capacitive deionization process could be used to remove low-level radioactive inorganic materials.

2. Treatment of boiler water in nuclear and fossil power plants. Such treatment is essential for the prevention of pitting, stress corrosion cracking, and scaling of heat transfer surfaces. Such a process may be particularly attractive for nuclear powered ships and submarines where electrical power is readily available and where there are space limitations, thereby restricting the inventory of chemicals required for regeneration of ion exchange resins.

3. Production of high-purity water for semiconductor processing. In addition to removing conductivity without the addition of other chemical impurities, the system is capable of removing small suspended solids by electrophoresis. Furthermore, the organic impurities chemisorb to the carbon.

4. Electrically-driven water softener for homes. The present system would soften home drinking water without the introduction of sodium chloride. At the present time, domestic water softeners use sodium chloride to regenerate a bed of ion exchange resin. Downstream of the ion exchanger, reverse osmosis has to be used to remove the sodium chloride introduced during regeneration. People on low-salt diets require low-salt water. The present capacitive deionization system does not require salt additions for regeneration, does not have to be followed by a reverse osmosis system, and will also remove hazardous organic contaminants and heavy metals from the water.

5. Removal of salt from water for agricultural irrigation. The energy efficiency of such a process and the lack of troublesome membranes could make such a process a contender for treating water for irrigation purposes. Solar energy could be used to power the low-voltage, low-current capacitive deionization plants.

6. Desalination of sea water. Such an application can be accomplished using the present separation method and system.

By using the separation systems according to the present invention, it is now possible to remove organic and inorganic contaminants and impurities from the liquid streams by the following physiochemical processes: the reversible electrostatic removal of organic or inorganic ions from water or any other dielectric solvent; the reversible or irreversible removal of any organic or inorganic impurity by any other adsorption process, including but not limited to underpotential metal deposition, chemisorption, and physisorption; the removal of any organic or inorganic impurity by electrodeposition, which could involve either electrochemical reduction or electrochemical oxidation; and the electrophoretic deposition and trappings of small suspended solids, including but not limited to colloids, at the surface of the electrodes. It is recognized that induced electric dipoles will be forced to the electrode surfaces by the imposed electric field.

More specific applications for the inventive system and process include any application where the capacitive deionizer is used to assist a gas scrubbing column; for example, if CO_2 were removed from a gas stream into an aqueous stream, it would convert into HCO_3^- and CO_3^{2-}. These ions could be removed from the scrubbing solution by capacitive deionization. Such applications include any large scale parallel use of the capacitive deionizer to assist in load leveling applications since it is recognized that the present invention can simultaneously serve as an energy storage device. Other applications include analytical instruments that combine the principles of capacitive deionization and ion chromatography, and chromatographic instruments based upon ion adsorption on carbon aerogel electrodes, either monolithic or powder beds.

Briefly, the above and further features and advantages of the present invention are realized by a new electrochemical cell for capacitive deionization and electrochemical purification and regeneration of electrodes. The cell includes two oppositely disposed, spaced-apart end plates, one at each end of the cell, as well as two generally identical single-sided end electrodes, that are arranged one at each end of the cell, adjacent to the end plates. An insulator layer is inter-

posed between each end plate and the adjacent end electrode.

Each end electrode includes a single sheet of conductive material having a high specific surface area and sorption capacity. In the preferred embodiment, the sheet of conductive material is formed of carbon aerogel composite. The cell further includes a plurality of generally identical double-sided intermediate electrodes that are equidistally separated from each other, between the two end electrodes. As the electrolyte enters the cell, it flows through a continuous open serpentine channel defined by the electrodes, substantially parallel to the surfaces of the electrodes. By polarizing the cell, ions are removed from the electrolyte and are held in the electric double layers formed at the carbon aerogel surfaces of the electrodes. As the cell is saturated with the removed ions, the cell is regenerated electrically, thus significantly minimizing secondary wastes. Additional embodiments of the present will hereafter be described in detail.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features of the present invention and the manner of attaining them, will become apparent, and the invention itself will be best understood, by reference to the following description and the accompanying drawings, wherein:

FIG. 1 is a diagrammatic view of a model desalination system according to the prior art;

FIG. 2 is an enlarged schematic, isometric, elevational view of a cell used in the model desalination system of FIG. 1;

FIG. 3 is a schematic, sectional, elevational view of an electrochemical cell which is constructed according to the present invention;

FIG. 4A is a greatly enlarged top plan view of a capacitive electrode according to the present invention, adapted for use in the electrochemical cell of FIG. 3;

FIG. 4B is a greatly enlarged exploded view of a rubber gasket used in conjunction with the capacitive electrode of FIG. 4A;

FIG. 5 is a block diagram of a first embodiment of a capacitive deionization-regeneration system using one electrochemical cell shown in FIG. 3;

FIG. 6 includes three superposed timing charts illustrating the operation of the capacitive deionization-regeneration system of FIG. 5;

FIG. 7 is a block diagram of a second embodiment of the capacitive deionization-regeneration system using two parallel electrochemical cells, each formed of stacks of numerous electrodes, shown in FIG. 3;

FIGS. 8(A–C) includes three timing charts A, B and C illustrating the operation of the, capacitive deionization-regeneration system of FIG. 7;

FIG. 9 is a timing chart illustrating the energy saving mode of the system shown in FIG. 7;

FIG. 10 is a block diagram representation of a third embodiment of a deionization-regeneration system according to the present invention;

FIG. 11 is schematic isometric view of another embodiment of an electrochemical cell according to the present invention, which is also adapted for use as part of the capacitive deionization-regeneration systems of FIGS. 5 and 7; and

FIGS. 12 through 14 represent empirical timing charts using the capacitive deionization-regeneration system of FIG. 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, and in particular to FIG. 3 thereof, there is illustrated an electrochemical cell 30 which is constructed according to the present invention. The cell 30 generally includes two oppositely disposed, spaced-apart end plates 31 and 32, one at each end of the cell 30, and two generally identical single-sided end electrodes 35, 36, one at each end of the cell 30, adjacent to the end plates 31 and 32, respectively. An insulator layer 33 is interposed between the end plate 31 and the end electrode 35. Similarly, an insulator layer 34 is interposed between the end plate 32 and the end electrode 36. Each single-sided electrode 35, 36 includes a single sheet of carbon aerogel composite bonded to one side of a titanium sheet with a conductive epoxy. Other appropriate bonding material can alternatively be used.

A plurality of generally identical double-sided intermediate electrodes (i.e., 37 through 43) are spaced-apart and equidistally separated from each other, between the two end electrodes 35, 36. Each double-sided electrode, i.e., 37, includes two sheets of carbon aerogel composite bonded to both sides of a titanium sheet with conductive epoxy. While FIG. 3 illustrates only seven double sided intermediate electrodes 37 through 43, it should become apparent to those skilled in the art that a different number of intermediate electrodes can alternatively be used without departing from the scope of the present invention. For instance, it would be possible to expand the capacity of the cell 30 to accommodate at least 192 intermediate electrodes, such that the total anode (or cathode) surface area is approximately 2.7×10^8 cm^2. Ultimately, the system could be expanded to include an unlimited number of electrode pairs.

The end electrodes 35, 36 and the intermediate electrodes 37 through 43 are generally similar in design, construction and composition, with the difference that each intermediate electrode has two sheets of carbon aerogel composite bonded to both sides of a titanium sheet with conductive epoxy, whereas each end electrode has only one sheet of carbon aerogel composite bonded to one side of a titanium sheet with conductive epoxy. It is recognized that other porous conductive, monolithic materials can be used in lieu of the carbon aerogel composite. For brevity, only one single-sided end electrode, i.e., 35, will now be described in more detail in connection with FIGS. 4A and 4B.

FIG. 4A is a greatly enlarged top plan view of the end electrode, which includes a generally flat, thin rectangularly shaped, corrosion resistant, metallic (i.e., titanium) sheet, structural support 40. A tab 42A extends integrally from one side of the structural support 40, for connection to the appropriate pole of a D.C. power source (not shown). A thin sheet 44 of high specific area, porous, conductive, monolithic material (i.e., carbon aerogel composite) is bonded to the surface of the structural support 40, and is suitable to be either a cathode or an anode. In this particular example, it will be presumed that the end electrode 35 is an anode. The structural support 40 further includes a series of generally identical apertures 47 for providing a passage to the electrolyte, through the end electrode 35.

In the preferred embodiment, the thin layer of high specific area material 44 is composed of a composite material formed by impregnating a carbon cloth with carbon aerogel, wherefore, the thin layer 44 will also be

referred to as carbon aerogel composite electrode 44. The new use of this carbon aerogel composite electrode 44 relies primarily on the unique open-cell nanostructure of the carbon aerogel material, including its interconnected porosity, ultrafine pore sizes and huge surface area. This carbon aerogel composite material is described in more detail in an article entitled *Carbon Aerogel Composite Electrodes*, by Joseph Wang et al., in Anal. Chem. 1993, vol. 65, pages 2300–2303, and in several articles and patents authored by Richard W. Pekala et al., such as U.S. Pat. No. 5,260,855 entitled Supercapacitors Based on Carbon Foams, which are incorporated herein by reference.

Carbon aerogels were developed at Lawrence Livermore Notional Laboratory, and are synthesized by the polycondensation of resorcinol and formaldehyde (in a slightly basic medium), followed by supercritical drying and pyrolysis (in an inert atmosphere). This fabrication process results in unique open-cell carbon foams that have high porosity, high surface area (400–1000 m²/g), ultrafine cell/pore sizes (less than 50 nm), and a solid matrix composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of 10 nm. The porosity and surface area of aerogels can be controlled over a broad range, while the pore size and particle size can be tailored at the nanometer scale. The carbon aerogels further offer both low density and ultrasmall cell size.

The use of the carbon aerogel composite electrode 44 presents a significant improvement over conventional devices, since in these latter devices only part of the specific area is effective for removing ions, and the remaining area is not effective because of the potential gradients across the electrodes. By using thin sheets of carbon aerogel composite as electrodes 44, substantially the entire surface area of these monolithic microporous electrodes is effective in the removal of ions, due to the desirable potential distribution in the aerogel.

While the best mode of the present invention utilizes thin sheets of carbon aerogel composite as electrodes, it should be apparent to those skilled in the art that beds of carbon aerogel particles can alternatively be used to form electrodes. Such beds of carbon aerogel particles have much higher specific area and sorption capacity than beds of conventional carbon powder, and therefore they are superior electrodes for capacitive deionization.

Returning now to FIG. 3, the end electrodes 35, 36 and the adjacent intermediate electrodes 37 through 43 are separated by means of thin sheets of insulating material, such as rubber gaskets 50 through 56. Each gasket has a large, square aperture in the center to accommodate adjacent carbon aerogel composite electrodes 44. As shown in FIGS. 4A and 4B, the structural support 40 includes a plurality of peripheral holes 48, such that when the cell 30 is to be assembled, the peripheral holes 48 are coaligned with corresponding peripheral holes in the insulation layers 33, 34 and the rubber gaskets 50 through 56, and a plurality of threaded rods 58, 59 are inserted through these coaligned holes, and are tightened by conventional means, such as nuts 60 through 63. Non-compressible, insulating, hollow, cylindrical spacers or compression rings 50A can be inserted in the peripheral holes of the rubber gaskets 50 through 56, and used to control the spacing of adjacent electrodes. A plurality of compression sleeves, i.e., 64A, 64B can be added to provide additional force for sealing.

While only two threaded rods 58, 59 are shown in FIG. 3 for illustration purpose, in this particular example, eight threaded rods are used to tighten the cell 30 to a leak proof state. These eight rods are designed to fit through the eight peripheral holes 48 in the structural support 40, as well as through the corresponding peripheral holes in the rubber gaskets 50 through 56 fitted with hollow-cylindrical spacers 50A (FIG. 4B).

Once the cell 30 is assembled, a plurality of chambers 65 through 71 are formed between the end and intermediate electrodes 35 through 43. These chambers 65 through 71 are adapted to fluidly communicate with each other via a plurality of apertures 73 through 79 in the structural supports of the intermediate electrodes 37 through 43, respectively. These apertures 73 through 79 are not coaligned, and may be either holes or slits. They are so positioned so that the fluid path therethrough, within the chambers 65 through 71, is forced to flow across all the exposed surfaces of the carbon aerogel composite electrodes 44. Referring to FIG. 3, the fluid first flows from left-to-right, then from right-to-left, an so on.

In operation, and merely for illustration purpose, the anodes and the cathodes of the cell 30 are interleaved in an alternating way. In this respect, every other electrode is an anode, starting with the end electrode 35, and ending with the intermediate electrode 43, and the remaining intermediate electrodes 37, 39, 41, 42 and the end electrode 36 are cathodes. As such, each pair of adjacent electrodes (anode and cathode) forms a separate capacitive deionization/regeneration unit.

The stream of raw fluid or electrolyte to be processed enters the cell 30 through a plurality of superposed, coaxially registered, generally circularly or rectangularly shaped openings, including an aperture 80 in the end plate 31, one or more apertures 82 in the insulation layer 33, and the apertures 47 in the end electrode 35. The fluid flows through the first chamber 65 as indicated by the arrow A, substantially parallel to the electrode surface. By polarizing the first deionization/regeneration unit, ions are removed from the fluid stream electrostatically, and are held in the electric double layers formed at the carbon aerogel surfaces of the electrodes 35 and 37. This will purify the fluid stream, at least partially.

The fluid stream then flows through the aperture 73 into the next chamber as indicated by the arrow B, where additional ions are removed by the polarization of the second deionization/regeneration unit 81 formed by the intermediate electrodes 37 and 38, thus further purifying the fluid stream. The fluid stream continues to travel through the remaining deionization/regeneration units, as indicated by the arrows C through G, and is progressively purified. Thereafter, as indicated by the arrow H, the purified fluid stream exits the cell 30 via a plurality of coaxially aligned apertures 90, 91, 92 in the end electrode 36, insulator layer 34, and the back plate 32, respectively.

The fluid stream leaving the cell 30 is purified since the contamination ions have been removed and collected by the cell 30. It should also become clear that one important characteristic of the novel configuration of the cell 30 is that the fluid stream does not flow through the porous electrodes, but rather in an open channel, with a relatively low pressure drop, and with minimal energy consumption for pumping. The energy expended to operate the cell 30 is minimal. In this respect, the fluid stream does not necessarily need to be

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pressurized by a pump to cause it to flow through the cell 30; gravity can be used, if desired.

Also, if the inventive deionization process were used for water desalination, the energy expended is that which is necessary to remove salt from water, whereas in conventional desalting processes, such as evaporation and reverse osmosis, the energy is expended to remove the water from salt. As a result, the present process is orders-of-magnitude more energy efficient than conventional processes.

Additionally, the pressure drop in the capacitive deionization cell 30 is insignificant compared to that needed for reverse osmosis. Also, contrary to conventional deionization processes, the electrodes have a very high and immobilized specific surface area and a high removal efficiency, and the carbon aerogel particles are not entrained by the fluid stream.

As the capacitive deionization cell 30 is saturated with the removed ions, the capacitive units become fully charged, and a sensor (not shown) indicates that such condition has been reached, and that the cell 30 is ready for regeneration. Contrary to conventional chemical regeneration processes, the present regeneration process is carried out electrically, thus eliminating the secondary wastes. The regeneration process takes place by disconnecting the power supply, by interconnecting the anodes and the cathodes, by electrically discharging all electrodes 35 through 43, and by flowing a suitable fluid stream of water or another suitable solution through the cell 30, along the same path described above in connection with the deionized stream of raw fluid. As a result, the capacitive units are discharged through, and release the previously removed ions into the flowing fluid stream, until the cell 30 is fully regenerated. At which time, the regeneration process is stopped and the deionization process restarts. The timing control of the deionization-regeneration process could be manual or automated.

Considering now the components of the cell 30 in more detail, the overall shape and dimensions of the cell 30 are determined by the mode of use and application of the capacitive deionization systems 111 and 175 illustrated in FIGS. 5 and 7, respectively. In the preferred embodiment, the end plates 31 and 32 are identical, rectangularly shaped, and made of 316 stainless steel or another appropriate corrosion resistant alloy. The end plates, unlike the electrodes, are not polarized. However, it should become clear that other shapes are also contemplated by the present invention. For instance, if the cell 30 were cylindrically shaped, the end plates 31 and 32 are circular, or if the cell 30 were conically shaped, one of the end plates 31, 32 can have a smaller size than the other plate, and the size of the electrodes therebetween gradually increases from one end plate to the other.

The insulator layers 33 and 34, as well as 50 through 56 are preferably made of an elastic, compressible, insulating, non-leachable material. Foe example, Teflon, Viton, Neoprene and similar materials are suitable materials for specific applications.

However, other suitable materials are also contemplated by the present invention. The structural supports 40 (FIGS. 4A, 4B) of the end electrodes 35, 36 and the intermediate electrodes 37 through 43 are preferably made of titanium, or, alternatively they can be selected from a suitable group of materials such as coated, corrosion-resistant, iron-chromium-nickel based alloys. Suitable coatings include gold, platinum, iridium, platinum-

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iridium alloys, or other similarly corrosion resistant materials.

In one example, the back plates are similarly sized and rectangularly shaped, and have the following dimensions: length 8.38 cm; width 7.87 cm; and thickness 0.16 cm. However, other dimensions can alternatively be used. The tab 42A extends integrally from the structural support 40, and is generally, but not necessarily rectangularly shaped. In the above example, the tab 42A has the following dimensions: length 1.78 cm; width 2.03 cm; and thickness 0.16 cm. This tab 42A is used to make electrical connection with the electrode.

As shown in FIGS. 4A and 4B, the structural support 40 includes a plurality of (in this example eight) peripheral holes 48 through which the threaded rods, i.e., 58, 59 pass, for aligning the electrodes 35 through 43. Several elongated apertures 47 are shown co-aligned outside, along, and adjacent to one side 105 of the sheets of aerogel carbon composite 44. These apertures 47 are sized so as to distribute the flow uniformly across the sheet of carbon aerogel composite with minimal pressure drop. It should also become clear that the number, position and size of these apertures 47 can vary with the desired mode of use and application of the cell 30.

Considering now the carbon aerogel composite electrode 44 in greater detail in connection to FIGS. 4A and 4B, it is shown as having a square shape, and as being centrally positioned relative to the structural support 40. In the present example, the carbon aerogel composite electrode 44 has a side dimension of 6.86 cm, a projected area of 23.5298 cm^2, and a thickness of about 0.0127 cm. Other shapes of the electrode 44 are also contemplated by the present invention. For instance, the electrode 44 can be circular, rectangular, or triangular.

While, as described above, the electrode 44 is preferably made of carbon aerogel, composite, any monolithic, porous solid that has sufficient electrical conductivity and corrosion resistance (chemical stability) to function as an electrode, can alternatively be used. Such alternative materials include porous carbon electrodes typically used in fuel cells, reticulated vitreous carbon foams, porous metallic electrodes made by powder metallurgy, porous electrodes made by microfabrication techniques, including photolithography, electroforming, physical vapor deposition (evaporation, sputtering, etc.) and etching, and conductive sponges of any type.

The electrode 44 could also be fabricated as a packed bed of carbon aerogel particles, having significantly higher specific surface area than the conventional packed carbon bed described in the Department of Interior Report and the Newman Article discussed above. This design offers the advantage of greatly enhanced capacity for electrosorption of ions, adsorption of organics, and capture of fine particles, but would require flow through porous media.

In the example illustrated in FIG. 3, the chambers 65 through 71 have a volume of about 300 ml, which corresponds to the minimum possible liquid volume required for regeneration. In other embodiments, the chambers 65 through 71 can have different volumes, such that the minimum possible liquid required for regeneration can be further reduced.

Turning now to FIG. 5, there is illustrated a block diagram of a first embodiment of a capacitive deionization-regeneration system 111 according to the present invention. The system 111 generally includes one or a

stack of sequential (i.e., serially) electrochemical cells 30 (FIG. 3), an electrical circuit 112, and a fluid circuit 114, such that the fluid circuit 114 regulates the flow of the fluid stream through the cell 30, under the control of the electrical circuit 112.

Considering now the electrical circuit 112, it includes a voltage controlled D.C. power supply 117 which provides a constant D.C. voltage across the adjacent pairs of electrodes 35 through 43 (FIG. 3). A resistive load 120 and a switch 121 are connected in parallel, across the positive and negative terminals 122A, 122B, respectively, of the power supply 117, and are used to discharge, or regenerate the single electrochemical cell 30.

The electrical circuit 112 further includes a control system, as a triggering device to initiate regeneration. This control system utilizes on-line conductivity cells, ion selective electrodes, pH electrodes, polarographic sensors, impedance sensors, optical transmission cells, and light scattering sensors. The components that can be triggered by this on-line control system include power supplies, valves and pumps.

A differential amplifier 126 is connected across a shunt resistor 118, and is further connected to an analog-to-digital converter 127 and a computer 128. The shunt resistor 118 is used to measure the current flowing from the power supply 117 to the cell 30, for monitoring and control. The differential amplifier 126 amplifies the voltage across the shunt resistor 118 to a level that is monitorable by the analog-to-digital converter 127 and the computer 128. Another differential amplifier 125 is connected across the terminals 122A, 122B of the power supply 117, via the shunt resistor 118, and operates as a buffer between the power supply 117 and the analog-to-digital converter 127, for protecting the analog-to-digital converter 127.

The differential amplifier 125 is connected across the terminals of the cell 30, and serves as a buffer between the cell 30 and the A/D converter 127. In operation, as the cell 30 is used to deionize the electrolyte, the switch 121 is open. In order to start the regeneration process, the power supply 117 is turned off, or disconnected, and the switch 121 is closed, for providing a path for the discharge current.

The analog-to-digital converter 127 is connected to the inlet stream of the fluid circuit 114, via a plurality of sensors, such as a thermocouple 134, a conductivity probe 135, and a pH sensor 136, via respective transducers 131, 132 and 133. The thermocouple 134 enables the monitoring of the temperature of the inlet stream, in order to prevent the overheating of the electrolyte, and further enables the calibration of the conductivity probe 135. The conductivity probe 135 is an on line sensor which permit the monitoring of the conductivity of the inlet stream. The pH sensor measures the pH level of the inlet stream. The transducers 131, 132 and 133 convert the measurements of the thermocouple 134, conductivity probe 135 and pH sensor 136 into voltages that are readable by and compatible with the analog-to-digital converter 127. A flow rate meter 154 measures the flow rate of the inlet stream.

The fluid circuit 114 includes a feed and recycle tank 150 which contains the raw fluid to be processed by the cell 30. It should be understood that the fluid stored in the feed and recycle tank 150 can be replaced with a continuous inflow of raw fluid. A valve 151 is fluidly connected between the feed and recycle tank 150 and a pump 152. The speed of the pump 152 is used to control

the flow rate of the inlet stream to the cell 30. The outlet stream is respectively connected, via two valves 156, 157, to a product tank 160 for storing the purified fluid, and to the feed and recycle tank 150. Valves 156 and 157 are used to select the mode of operation: batch mode or complete recycle; continuous mode or once through.

Similarly to the inlet stream, the analog-to-digital converter 127 is also connected to the outlet stream of the fluid circuit 114, via three transducers 141, 142, 143, a thermocouple 144, a conductivity probe 145, and a pH sensor 146.

In the continuous mode of operation, the raw fluid or electrolyte to be deionized is initially stored in the feed and recycle tank 150, and the valve 157 is closed. The pump 152 is activated for pumping the fluid from the feed and recycle tank 150 to the cell 30, where the fluid stream is deionized and purified, as described above. The purified effluent is then routed to the product tank 160 via the open valve 156. In certain applications, it would be desirable to recycle the fluid stream more than once, in order to obtain the desired level of purification. In which case, the valve 156 is closed, and the valve 157 is opened, in order to allow the fluid stream to be recycled through the cell 30.

When the cell 30 is saturated, the deionization process is automatically interrupted and the regeneration process starts. For this purpose, the power supply 117 is disconnected, and a regeneration tank (not shown) is fluidly connected to the pump 152 and the cell 30. The regeneration tank contains a suitable regeneration solution (only a relatively small amount of regeneration solution is needed and can have the same composition as the feed stream, for instance raw water), or alternatively, pure water can be used. The regeneration solution is passed through the cell 30, and the regeneration process takes place by placing the removed ions back into the regeneration solution.

In the event the electrodes become saturated with organic contaminants, it is possible to clean and regenerate the carbon composite electrode 44, or other porous monolithic electrodes by passing solutions of chemically and electrochemically regenerated oxidants, including but not limited to Ag(II), Co(III), Fe(III), ozone, hydrogen peroxide, and various bleaches, through the electrochemical cell 30.

FIGS. 12 through 14 represent empirical timing charts using the capacitive deionization-regeneration system 111 of FIG. 5.

FIG. 6 includes three superposed timing charts A, B, C, illustrating the operation of the capacitive deionization-regeneration system 111 of FIG. 5, used for the deionization and regeneration of 100 micromho of NaCl solution. Chart A represents the conductivity of the electrolyte, and includes two curves, one illustrating the inlet stream conductivity and the other curve illustrating the outlet stream conductivty. Chart B represents the current flowing through the cell 30. Chart C represents the voltage across the cell 30. T represents the deionization-regeneration cycle.

FIG. 7 illustrates a second embodiment of the capacitive deionization-regeneration system 175 using at least two parallel electrochemical cells 30A and 30B, both similar to the cell 30 shown in FIG. 3. FIG. 8 illustrates an exemplary operation of the capacitive deionization system 175 using 100 micromhos NaCl solution. One of the main advantages of the system 175 is its ability to maintain a continuous deionization and regeneration

operation. The system 175 is generally similar to the system 111, and uses two cells 30A and 30B, such that when one cell 30A or 30B is deionizing the fluid stream while the other cell is regenerating, in preparation for the deionization process. Therefore, the operation of the system 175 is cyclical and continuous. For each one of the cells 30A and 30B, each cycle includes two half cycles. The first half cycle being the deionization process, and the second half cycle being the regeneration process, such that the cycles of the cells 30A and 30B are essentially 180 degrees out of phase.

The system 175 includes a power supply and switching apparatus 176 connected across both cells 30A and 30B, for selectively operating these cells. For instance, while the preferred embodiment of the system 175 includes operating one cell for deionizing a fluid stream, while the other cell is simultaneously being regenerated, it should be understood that both cells 30A and 30B can simultaneously perform the same process, i.e., deionization or regeneration.

A controller 178 regulates a plurality of inflow and outflow valves 179, 180a, 180b, 180c, 181a, 181b, 181c, and 182, for controlling the flow of the fluid stream to and from the cells 30A and 30B. An analog-to-digital converter 185 converts measurement signals from a plurality of conductivity and ion specific sensors 187, 188 disposed along the fluid circuit of the system 175, and transmits corresponding digital signals to a computer 190, which controls the controller 178, the power supply and switching apparatus 176, and thus the overall operation of the system 175. While only two sensors 187, 188 are shown merely for illustration purpose, other sensors can also be included to provide additional feedback data to the computer 190.

The operation of the system 175 will now be further described in relation to FIG. 8. FIG. 8 includes three timing charts A, B and C illustrating the operation of the capacitive deionization-regeneration system 175 of FIG. 7. In this particular case, no electrical power released during the regeneration of one cell is used by the other cell for deionization. Chart A shows the conductivity (micromhos) versus time (seconds), of the effluent fluid streams flowing from the cells 30A and 30B. Chart B shows the current (amperes) flowing through the cells 30A and 30B. Chart C shows the voltage (volts) applied across each cell 30A, 30B. In the case of aqueous (water-based) streams, optimum performance is obtained with a voltage pulse having an amplitude of 0.6–1.2 volts. Lower voltages diminish the capacity of the electrodes while significantly higher voltages cause electrolysis and associated gas evolution from the electrodes. Merely for clarity purpose, the solid lines in these charts A, B, C, relate to the behavior of the cell 30A, while the phantom or broken lines relate to the behavior of the cell 30B.

Considering now Chart C, the solid line illustrates a series of square shaped voltage pulses 191, 192, 193 applied across the cell 30A, with a plateau value of about 1.2 volts, while the broken line illustrates a series of square shape voltage pulses 194, 195 applied across the cell 30B, also with a plateau value of about 1.2 volts. It should however be understood that different voltages can be applied. Specifically, in the case of aqueous streams, the preferred voltages range between 0.6 and 1.2 volts. The voltage pulses applied to cells 30A and 30B are 180 degrees out of phase.

The voltage pulse 191 in Chad C will cause the cell 30A to progress with the deionization process, as illus-

trated by the current curve 197 in chart B, and by the conductivity curve 198 in chart A. While the voltage pulse 191 in Chad C is applied across the cell 30A, the anodes and cathodes of cell 30B are connected together through an external load, causing cell 30B to regenerate, as illustrated by the current curve 199 in chart B, and by the conductivity curve 200 in chart A.

Thereafter, the voltage pulse 194 is applied across the cell 30B causing it to progress with the deionization process, as illustrated by the current curve 201 in chart B, and by the conductivity curve 202 in chart A. While the pulse 194 is applied across the cell 30B, the anodes and cathodes of cell 30A are connected together through an external load, causing cell 30A to regenerate, as illustrated by the current curve 203 in chart B, and by the conductivity curve 204 in chart A.

The foregoing deionization-regeneration cycle enables the system 175 to operate continuously without interruption, since, as one of the cells 30A, 30B becomes saturated, the other cell is almost or completely regenerated, and is ready to proceed with the deionization process. As a result, the purified fluid stream at the output of the system 175 is continuous. The operation of the system 175 might be particularly attractive in nuclear power plants for scavenging contaminants from boiler water.

To briefly summarize the operation of the system 175, during the deionization process, the corresponding cell, either 30A or 30B, capacitively charges the electrode pairs forming it, thereby removing ions from the fluid stream passing through it. At the beginning of the deionization process, the cell has been completely and electrically discharged; at the end of the deionization process, the cell has been completely and electrically charged. Subsequently, during the regeneration process, the corresponding cell, either 30A or 30B, capacitively discharges the electrode pairs forming it, thereby placing ions into the fluid stream passing through it, greatly increasing the concentration of ions in that stream. At the beginning of the regeneration process, the cell has been completely and electrically charged; at the end of the regeneration process, the cell has been completely and electrically discharged.

FIG. 9 illustrates another characteristic of the present invention, namely an enhanced energy efficiency or energy saving mode. In this particular mode of operation, a timing chart is used to illustrate the potential across each of the cells 30A and 30B, where the solid lines relate to the behavior of the cell 30A, while the broken lines relate to the behavior of the cell 30B. Starting at time t_0, the cell 30B is fully charged and ready to be regenerated, while the cell 30A is fully discharged and ready to begin the deionization process.

While it would be possible to disconnect the cell 30B from the power supply 176, and to connect the power supply 176 to the cell 30A, it is now possible to save energy, and in certain applications, save a significant fraction of the energy required to operate the system 175. According to the present invention, at time t_0, the cells 30A and 30B can be connected, such that cell 30B is discharged through the cell 30A, as indicated by the curve 210, causing the cell 30A to be charged, as indicated by the curve 211. Electrical energy stored in the cell 30B is used to power the cell 30A during deionization in the cell 30A.

As soon as an equilibrium voltage is reached, i.e., approximately 0.6 volts at time t_1, the cell 30A is connected to the power supply 176 so that the charging

process can be completed, as illustrated by the curve 212. Simultaneously, the cell **30B** is completely discharged through an external load, as indicated by the curve 213. As a result, a significant portion of the energy required to charge the cell **30A** is generated by the cell **30B**, with the remaining energy supplied by the power supply **176**.

Thereafter, at time t_2, the cell **30A** is fully charged and is ready for regeneration, while the cell **30B** is completely discharged, and is ready for the deionization process. The cells **30A** and **30B** are then connected, such that the cell **30A** is discharged through the cell **30B**, as illustrated by the curve 214, while the cell **30B** is charged, as illustrated by the curve 215.

As soon as the equilibrium voltage is reached at time t_3, the cell **30B** is connected to the power supply **176** so that the charging process can be completed, as illustrated by the curve 216, and the cell **30A** is allowed to completely discharge through an external load, as illustrated by the curve 217. As a result, a significant portion of the energy required to charge the cell **30B** is generated by the cell **30A**, with the remaining energy supplied by the power supply **176**.

Turning now to FIG. 10, it is a block diagram representation of a third embodiment of a deionization-regeneration system **220** according to the present invention. The system **220** includes a matrix of systems **222, 224, 226** similar to the system **175** (FIG. 7), which are connected in series. Each system includes at least one pair of cells which are connected and which operate as described in relation to the system **175**. Thus, the system **222** includes cells **(1,1)** and **(1,2)**; the system **224** includes cells **(2,1)** and **(2,2)**; and the system **226** includes cells **(n,1)** and **(n,2)**. Each of the systems **222, 224** and **226** includes a power supply and switching system **176A, 176B, 176C**, respectively, which is similar to the power supply and switching system **176** shown in FIG. 7.

In operation, when one cell i.e., **(1,1)** of the pair of cell, i.e., **222** is performing the deionization process, the other cell, i.e., **(1,2)** is being regenerated. It should become clear to those skilled in the art that while only three systems **222, 224** and **226**, each of which including two cells, are shown merely for illustration purpose, a different combination of systems or cells can be selected, without departing from the scope of the present invention.

One novel application for the system **220** is the progressive and selective deionization and regeneration feature. In other terms, different potentials (V_1, V_2, V_n) are applied across each system (**222, 224, 226**, respectively) in order to selectively deionize the influent fluid stream, by having each system (**222, 224, 226**) remove different ions from the fluid stream. Thus, in this particular example, $V_1 < V_2 < V_n$, such that the system **222** is capable of removing reducible cations such as Cu^{++}; the system **224** is capable of removing reducible cations such as Pb^{++}; and the system **226** is capable of removing non-reducible and non-oxidizable ions such as Na^+, K^+, Cs^+, Cl^-, or other similar ions, which remain in their ionic state.

By using the cells and systems according to the present invention, as described above, it is possible to remove the following impurities from aqueous streams and subsequently regenerate the cells:

1. Non oxidizable organic and inorganic anions. Inorganic anions include: OH^-, Cl^-, 1^-, F^-, NO_3^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, and

PO_4^{3-}, etc. In this case, the operative mechanism is electrostatic double layer charging. For this purpose, it would be desirable to maintain the terminal potential across the electrodes lower than that required for electrolysis of the solvent in order to avoid gas evolution. The optimum potential is in the range between 1.0 and 1.2 volts, relative to the normal hydrogen electrode (NHE). In general, the recommended range of potential for water treatment lies between 0.6 and 1.2 volts.

2. Non reducible cations, such as Li^+, Na^+, K^+; Cs^+, Mg^{++}, Ca^{++}, etc. Here too the operative mechanism is electrostatic double layer charging.

3. Reducible cations, such as: Cu^{++}, Fe^{++}, Pb^{++}, Zn^{++}, Cd^{++}, etc. In this case, the operative mechanism is electrodeposition.

4. Colloidal particles such as bacteria, viruses, oxide particles, dirt, dust, etc. In this case, the operative mechanism is electrophoresis.

5. Chemisorption of organic molecules onto the carbon composite electrode **44**. This adsorption process might be relatively irreversible. Regeneration in this case would involve the use of strong oxidants for the purposes of destroying the adsorbed organics (i.e., PCB).

One exemplary application of the present invention includes the design and manufacture of a deionization system for purifying radioactive water. For instance, one embodiment of the present system could be used to purify the waste water generated from washing fuel assemblies coated with metallic sodium residuals. The 500 gallons of waste water currently generated during the washing of each assembly include approximately 200 ppm sodium, trace quantities of other metals, trace quantities of some non-metal that can be removed by filtration, and trace quantities of radioactive constituents (primarily fuel cladding corrosion products). Grade B water purity would have to be achieved so that water could be recycled; (i.e., conductivity less than 20 microsiemens/cm).

Referring now to FIG. 11, it is a schematic isometric view of an electrochemical cell **250**, with a portion **252** thereof enlarged. The cell **250** can be adapted for use as part of the capacitive deionization-regeneration systems **111** and **175** of FIGS. 5 an 7, respectively. The cell **250** includes a plurality of electrodes **253, 254** that are separated by a porous separator or membrane **255**. The separator **255** is sandwiched between two adjacent electrodes **253, 254**, and allows an open channel to be formed and defined therebetween. The electrodes **253** and **254** are similar to the electrodes of cells **30, 30A** and **30B** described above. The electrodes **253, 254** and the separator **255** are rolled spirally together, so that the electrolyte flows in the open channels formed between the electrodes **253, 254**, and exits the cell **250** with minimal flow resistance. While the cell **250** has been described as including two electrodes **253, 254** and one separator **255** for illustration purpose, it should be understood that additional electrodes and separators can alternatively be used.

The foregoing description of the embodiments of the present invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms described, and obviously many other modifications are possible in light of the above teaching. The embodiments were chosen in order to explain most clearly the principles of the invention and its practical applications,

thereby to enable others in the art to utilize most effectively the invention in various other embodiments and with various other modifications as may be suited to the particular use contemplated.

What is claimed is:

1. An electrochemical cell comprising in combination:

two oppositely disposed, spaced-apart end plates, one at each end of the cell;

two generally identical single-sided end electrodes, one at each end of the cell, adjacent to said end plates;

an insulator layer interposed between one of said end plates and an adjacent one of said end electrodes;

an insulator layer interposed between the other end plate and the other one of said end electrodes;

each single-sided electrode including a single sheet of conductive material having a high specific surface area and sorption capacity; and

a plurality of generally identical double-sided intermediate electrodes being spaced-apart and equidistally separated from each other, between said two end electrodes.

2. The electrochemical cell according to claim 1, wherein said conductive material includes carbon aerogel composite.

3. The electrochemical cell according to claim 2, wherein each end electrode includes a sheet of carbon aerogel composite bonded to one side of a metallic structural support; and

wherein each intermediate electrode includes two sheets of carbon aerogel composite bonded to both sides of a metallic structural support.

4. The electrochemical cell according to claim 3, wherein the number of said plurality of intermediate electrodes is at least 192.

5. The electrochemical cell according to claim 3, wherein said metallic structural support includes a titanium sheet.

6. The electrochemical cell according to claim 3, wherein each metallic structural support includes a plurality of apertures for providing passage to an electrolyte, through said end electrodes and said intermediate electrodes.

7. The electrochemical cell according to claim 6, wherein said specific surface areas of carbon aerogel composite electrodes range between 400 and 1000 m^2/gm.

8. The electrochemical cell according to claim 6, wherein said end electrodes and said intermediate electrodes are separated by a plurality of thin insulating gaskets with central apertures.

9. The electrochemical cell according to claim 6, wherein each pair of adjacent electrodes forms an open chamber adapted to fluidly communicate with a subsequent chamber via said plurality of apertures in said structural supports.

10. The electrochemical cell according to claim 9, wherein said apertures are not coaligned, and are positioned so that the electrolyte therethrough is forced to flow across all the exposed surfaces of said sheets of carbon aerogel composite.

11. The electrochemical cell according to claim 10, wherein the electrolyte path within said chambers is serpentine.

12. The electrochemical cell according to claim 11, wherein said end electrodes and said intermediate electrodes form a plurality of anodes and cathodes;

wherein said anodes and cathodes are interleaved in an alternating way, such that every other electrode is an anode; and

wherein each pair of adjacent anode and cathode forms a separate capacitive deionization/regeneration unit.

13. The electrochemical cell according to claim 12, wherein the each chamber formed within each deionization/regeneration unit allows the electrolyte to flow through said unit along a path parallel to the surfaces of said electrodes forming said unit.

14. The electrochemical cell according to claim 13, wherein when said deionization/regeneration units progressively and electrostatically remove ions from the electrolyte during a deionization process; and

wherein said deionization/regeneration units progressively place the removed ions back into the electrolyte during the regeneration process.

15. The electrochemical cell according to claim 14, wherein the electrolyte flows through said deionization/regeneration units under the force of gravity.

16. The electrochemical cell according to claim 14, wherein the electrolyte is sea water; and

wherein the deionization process includes desalting the electrolyte.

17. The electrochemical cell according to claim 14, wherein each chamber has a volume which corresponds to the minimum possible liquid volume required for regeneration.

18. The electrochemical cell according to claim 1, wherein said conductive material includes carbon aerogel particles.

19. A capacitive deionization-regeneration system comprising in combination:

at least one electrochemical cell including:

a. two oppositely disposed, spaced-apart end plates, one at each end of the cell;

b. two generally identical single-sided end electrodes, one at each end of the cell, adjacent to said end plates;

c. an insulator layer interposed between one of said end plates and an adjacent one of said end electrodes;

d. an insulator layer interposed between the other end plate and the other one of said end electrodes;

e. each single-sided electrode including a single sheet of conductive material having a high specific surface area and sorption capacity; and

f. a plurality of generally identical double-sided intermediate electrodes being spaced-apart and equidistally separated from each other, between said two end electrodes; an electrical circuit for controlling the operation of the cell;

a fluid circuit for regulating the flow of and electrolyte through the cell, under the control of the electrical circuit.

20. The deionization/regeneration system according to claim 18 further including at least two parallel electrochemical cells in order to maintain a continuous deionization and regeneration operation.

21. An electrostatic method for deionizing an electrolyte comprising the step of passing the electrolyte through an electrochemical cell including:

a. two oppositely disposed, spaced-apart end plates, one at each end of the cell;

b. two generally identical single-sided end electrodes, one at each end of the cell, adjacent to said end plates;

c. an insulator layer interposed between one of said end plates and an adjacent one of said end electrodes;

d. an insulator layer interposed between the other end plate and the other one of said end electrodes;

e. each single-sided electrode including a single sheet of conductive material having a high specific surface area and sorption capacity; and

f. a plurality of generally identical double-sided intermediate electrodes being spaced-apart and equidistally separated from each other, between said two end electrodes.

22. The method according to claim 21, further including the step of automatically interrupting the deionization process when the cell is saturated.

23. The method according to claim 22, further including the step of automatically starting a regenerating process of the cell when the deionization process is interrupted.

24. The method according to claim 22, further including the steps of:

using at least two parallel electrochemical cells in order to maintain a continuous deionization and regeneration operation; and

operating a first one of said at least two cells for deionizing the electrolyte, while the other cell is simultaneously being regenerated.

25. The method according to claim 24, further including the steps of:

operating said at least two cells in an enhanced energy saving mode, whereby when either of said cells is fully charged and ready to be regenerated, the other cell is fully discharged and ready to begin the deionization process; and

electrically connecting said cells, at least until an equilibrium voltage is reached.

26. The method according to claim 21, wherein said step of passing the electrolyte includes the step of removing various ions from waste water.

27. The method according to claim 21, wherein said step of passing the electrolyte includes the step of treating boiler water in nuclear and fossil power plants.

28. The method according to claim 21, wherein said step of passing the electrolyte includes the step of producing high-purity water for semiconductor processing.

29. The method according to claim 21, wherein said step of passing the electrolyte includes the step of softening home drinking water.

30. The method according to claim 21, wherein said step of passing the electrolyte includes the step of removing salt from water for agricultural irrigation.

31. The method according to claim 21, wherein said step of passing the electrolyte includes the steps of:

removing impurities from an aqueous stream; and subsequently regenerating said cell.

32. The method according to claim 31, wherein the removed impurities include non oxidizable organic and inorganic anions.

33. The method according to claim 31, wherein the removed impurities include non reducible cations.

34. The method according to claim 31, wherein the removed impurities include reducible cations.

35. The method according to claim 31, wherein the removed impurities include colloidal particles.

36. The method according to claim 31, wherein the step of removing impurities includes chemisorption of organic molecules.

37. An electrochemical cell comprising in combination:

a plurality of electrodes separated by a plurality of porous separators interposed between two adjacent electrodes;

each one of said plurality of electrodes including a single sheet of conductive material having a high specific surface area and sorption capacity;

each of said plurality of separators defining an open channel between two adjacent electrodes; and

said plurality of electrodes separators being rolled spirally together, for allowing an electrolyte to flow in said open channel and to exit the cell with minimal flow resistance.

* * * * *

**Process for Removing Dissolved Contaminants from Aqueous Solutions
Using Getters and Reversibly Dispersible Carriers
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Date of Patent: January 7, 1992
Assignee: Tiegel Manufacturing Co., Belmont, California**

United States Patent [19]

Wegner

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[54] **PROCESS FOR REMOVING DISSOLVED CONTAMINANTS FROM AQUEOUS SOLUTIONS USING GETTERS AND REVERSIBLY DISPERSIBLE CARRIERS**

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[58] Field of Search 210/634, 638, 643, 725, 210/727, 728, 729, 912, 908, 909

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[57] **ABSTRACT**

A process for purifying contaminated aqueous solutions without using ion exchange resins or organic solvents is provided. The process comprises contacting an aqueous solution with a getter compound and a non-polymeric carrier compound in a dispersed state to remove dissolved contaminants or recover dissolved valuable materials. Suitable carrier compounds having pendant long chain hydrocarbon radicals and hydrophilic moieties are disclosed. The process is highly efficient and effective for removing a wide variety of dissolved contaminants such as metal ions, non-metal ions and dissolved organic contaminants such as dyes.

7 Claims, No Drawings

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PROCESS FOR REMOVING DISSOLVED CONTAMINANTS FROM AQUEOUS SOLUTIONS USING GETTERS AND REVERSIBLY DISPERSIBLE CARRIERS

FIELD OF THE INVENTION

The present invention relates to a process for removing contaminants or recovering valuable materials from aqueous solutions. More particularly, it relates to the efficient and effective removal of dissolved contaminants such as toxic metal ions from wastewater by utilizing getters and reversibly dispersible carriers.

BACKGROUND OF THE INVENTION

A significant problem in the chemical industry is the treatment of wastewater and other process streams to remove pollutants to environmentally acceptable levels. Millions of gallons of wastewater contaminated with heavy metals and other pollutants are generated each day which must be treated to reduce the amount of pollutants to very low levels. For example, particularly toxic pollutants such as lead and mercury must be reduced to 50 ppb and 2 ppb, respectively. The following Table I sets forth a list of "priority" pollutants established under the Clean Water Act and the current federal drinking water and maximum allowable river discharge limits.

TABLE I

EPA Priority Pollutant Elements	Maximum Allowable Concentrations (ppm)
Antimony	0.15
Arsenic	0.05
Beryllium	0.000037
Cadmium	0.01
Chromium	0.05
Copper	1.0
Lead	0.05
Mercury	0.002
Nickel	0.013
Selenium	0.01
Silver	0.05
Thallium	0.013
Zinc	5.0

The need to remove pollutants from large volumes to wastewater to these very low levels has pushed currently available technologies to their limits. Aside from the ability to achieve low levels of contamination, a number of other features are desired in a process for treating wastewater. It is important to be able to treat polluted water in a cost effective manner. In addition to cost effective operation of the process, it is desirable to minimize any required changes to existing water pollution equipment. It is also desirable to reduce the size of a treatment plant as much as possible by increasing the processing rate. In some cases, it is desirable to use a recyclable material to remove the pollutants, so long as the regeneration process does not create more pollution than it eliminates. A wastewater treatment process should create as little solid waste as possible. Finally, the process should not create additional pollution problems such as polluting the treated water with other environmental pollutants.

One of the most popular technologies for treating wastewater is based on a settling process using lime. Calcium hydroxide or magnesium hydroxide is added to the water in a settling tank to absorb the offending contaminant. This technology permits the processing of

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large volumes without adding polluting chemicals and uses very simple equipment. However, in many cases, the contaminant concentration cannot be reduced low enough to meet EPA standards without using excessive amounts of material and long processing times. Additionally, large amounts of solid hazardous waste in the form of sludge are produced which cannot be effectively regenerated. While landfill has been the most popular means of disposing of sludge, it is rapidly becoming an unacceptable method of handling hazardous waste. Thus, using this technology, the contaminated wastewater problem is essentially being replaced by a solid hazardous waste disposal problem.

Another popular method of cleaning contaminated wastewater is the use of ion exchange resins to filter out the contaminants. Generally speaking, the advantages of ion exchange resins are that it is regenerable, it does not pollute the treated water and usually no separation process is required to remove the ion exchange resin from the treated water. However, the use of ion exchange resins to treat wastewater has a number of disadvantages.

Ion exchange resin processes are slow, very expensive and have low efficiencies. In order to be effective, the wastewater must be passed through a significant amount of resin, usually in the form of a filter bed. This is acceptable for treating small volumes of water to achieve certain levels of purity (e.g., 0.1 ppm of lead). However, as the desired level of purity (e.g. 0.05 ppm of lead) and volume of water increase, this technology becomes increasingly slow or less effective. The complex fabrication process and sophisticated synthetic chemistry involved in developing and producing ion exchange resins significantly contributes to the expense of using ion exchange resins to purify liquid waste and limits the variety of resins available. Ion exchange resin beds may be regenerated, but the wastewater from the regeneration must be treated to remove bulk toxins and then usually passed through the ion exchange resin again to eliminate all the polluted water.

Another technology for removing water soluble material is solvent extraction. This technology is not used in the waste water treatment industry, but rather for reclaiming materials of value such as in the mining industry. In solvent extraction processes, an organic solvent such as kerosene is contacted with the water containing the material to be reclaimed. The organic solvent contains an extractant compound which is preferably highly soluble in the organic phase and significantly less soluble in the aqueous phase. The extractant compound complexes with the material to be removed and the complexed extractant-material remains dissolved in the solvent. The organic and aqueous phases are then separated such as by decanting. The primary advantages of solvent extraction are speed, effectiveness, and ease of regeneration. The extractant compounds are also generally easier to synthesize than ion exchange resins. Therefore, a much broader variety of materials is commercially available and extractants may be tailored to selectively extract particular materials. However, solvent extraction does have disadvantages that make this technology unsuitable for the purification of wastewater.

One major disadvantage is that solvent extraction leaves solvent and extractant residues in the processed water thus creating another pollution problem. The solvents and in some cases the extractants are environmentally toxic. The solvents are generally flammable

and toxic which creates an environmental hazard. They may also be expensive thereby contributing to the expense of the process. If regeneration cannot be used, it takes a large volume of solvent to treat a given volume of water and solvent extraction may be prohibitively expensive. While the solvents are easier to regenerate than ion exchange resin and yield a much smaller volume of regeneration waste, the wastes still must be treated, creating yet another pollution problem.

The process of the present invention has the advantages of the above technologies with few disadvantages and is also highly efficient and effective for purifying aqueous solutions. The same equipment that is commonly found in most large scale water and municipal water treatment plants (i.e., settling process equipment) may be used to practice the present process. For a given volume of wastewater, the processing time is generally much less than for ion exchange resins or settling and comparable with processing time for solvent extractions. However, unlike solvent extraction, potentially toxic and flammable solvents are not introduced into the water. Compared to lime settling treatment, very little sludge is produced, yet low contaminant concentrations that meet EPA regulations may be achieved. The getters and carriers used in the present process may be regenerated easily with inexpensive chemicals without producing excessive regeneration wastewater. Because relatively small amounts of sludge are generated and the getters and carriers are not usually expensive compounds, the wastes may optionally be disposed of by landfill or incineration.

SUMMARY OF THE INVENTION

The present invention provides a process for removing a dissolved contaminant from an aqueous solution comprising: contacting the aqueous solution with a getter and a non-polymeric, reversibly dispersible carrier in a dispersed state to form a getter-contaminant material; removing the getter-contaminant material by reducing the dispersibility of the carrier to form a discontinuous phase containing the getter-contaminant material and separating the discontinuous phase from the aqueous solution.

A process for purifying contaminated aqueous solutions without using ion exchange resins or organic solvents is provided. The process comprises contacting an aqueous solution with a getter compound and a non-polymeric carrier compound in a dispersed state to remove dissolved contaminants or recover dissolved valuable materials. Suitable carriers having pendant long chain hydrocarbon radicals and hydrophilic moieties are disclosed. The process is highly efficient and effective for removing a wide variety of dissolved contaminants such as metal ions, non-metal ions and dissolved organic contaminants such as dyes.

DETAILED DESCRIPTION OF THE INVENTION

According to the process of the present invention, a getter and a reversibly dispersible carrier are contacted with a contaminated aqueous solution in a dispersed state. The getter and dissolved contaminant form a getter-contaminant material which is believed to be in the form of a complex. The getter-contaminant material is then removed by reducing the dispersibility of the carrier in the aqueous solution to form a discontinuous, preferably solid, phase which may be separated from the aqueous solution.

The process of the present invention is useful to remove a wide variety of dissolved contaminants such as aluminum, antimony, arsenic, beryllium, boron, cadium, cesium, chromimum, cobalt, copper, iron, lead, mercury, nickel, plutonium, selenium, silver, thallium, uranium, vanadium, zinc, and the like and dissolved organic contaminants such as polychlorinated biphenyls (PCBs), trichloroethylene, DDT, fluoroscene, trihalomethanes, trihalomethane precursors, dyestuffs such as methylene blue and the like. The process may also be used to recover dissolved valuable metal, non-metal and organic ions.

A "reversibly dispersible carrier" is a non-polymeric compound which is substantially insoluble in water having at least one pendant hydrophobic moiety and at least one hydrophilic moiety. The pendant hydrophobic moiety is preferably a long chain (C_{14}-C_{32}, more preferably C_{18}-C_{32}) n-alkyl group and most preferably a stearyl group. When more than one pendant hydrophobic moiety is present, the total number of carbon atoms on these moieties should be preferably 16 or greater. Thus, two pendant C_{10} straight chain hydrocarbon radicals will generally impart sufficient hydrophobicity. Suitable carriers include, for example, stearic acid, stearyl phosphate, distearyl phosphate, stearyl amine, the like and mixtures thereof.

A suitable carrier must be sufficiently water insoluble so that excessive amounts of the carrier compound do not dissolve in the aqueous solution. However, the carrier must also be dispersible on an essentially molecular level in water so that it may be placed in a dispersed state. It has been found that while polymers having complexing moieties such as ion exchange resins are highly water insoluble, they are not readily dispersible because of their high molecular weight. In contrast, the carrier compounds used in the present process are both substantially water insoluble and dispersible. These carriers are generally not useful in solvent extraction, because they have poor solubility ($<2\%$) in typical hydrocarbon solvents.

While not being bound by any particular theory, it is believed that the pendant long chain hydrocarbon radicals such as stearyl radicals impart high water insolubility to the carriers while permitting the carriers to be highly dispersed in water. Thus, these carrier compounds are dispersible on an essentially molecular level. The carrier may be analogized as having a "soap-like tail" covalently bonded directly to the hydrophilic moiety or to a linking group which is bonded to a hydrophilic moiety. It is believed that the hydrophobic moiety of the carrier molecule has an affinity for the hydrophobic moiety of the getter molecule which causes the getter to be dispersed and coagulated with the carrier in the present process.

A "getter" is a non-polymeric, substantially water insoluble compound having at least one pendant hydrophobic moiety and at least one ion complexing moiety. The complexing moiety is preferably an ion having an affinity for the contaminant ion desired to be removed from the aqueous solution. The pendant hydrophobic moiety may be a substituted or unsubstituted alkyl, cycloalkyl, alkoxyalkyl, alkycycloalkyl, aryl, alkylaryl, aralkyl and cycloalkylaryl, preferably unsubstituted branched or straight chain alkyl, radical having 1-32 carbon atoms. Generally, extractants known in solvent extraction processes may be used as getters in the process of the present invention.

Suitable getters include, for example, dithiophosphinates such as bis (2,4,4-trimethylpentyl) dithiophosphinate, diisobutyldithiophosphinate, di-2-ethylhexyl dithiophosphinate; phosphates such as di-2-ethylhexyl phosphate, tributyl phosphate; dithiophosphates such a dicyclohexyl dithiophosphate; amines; sulfides; sulfonates; carbamates; dithiocarbamates such as bis-dimethyl-thiocarbamoyl monosulfide, bis-diethyl-thiocarbamoyl disulfide, bis-pentamethylene-thiocarbamoyl tetrasulfide, bis-dimethyl-thiocarbamoyl disulfide; the like and mixtures thereof.

Table II below summarizes the efficiency, effectiveness, and speed that the various technologies have in treating the same volume of water.

K_f is a measure of the relative efficiency of various processing materials. It assumes a linear relation between the amount of material used and the amount of metal taken out. The larger the K_f is, the more water a given amount of getter can treat and still remove the contaminant to a certain level.

$$K_f = \frac{[\text{Weight of metal removed}]}{[\text{Weight of material used}] \times [\text{Weight of metal remaining}]} \times 100,000$$

A large K_f indicates high efficiency. Getters and carriers which impart a K_f of 20,000 or greater to the process of the present invention are preferred.

K_{ft} is a measure of the relative amount of water that can be processed in the same amount of time assuming a given K_f efficiency:

$$K_{ft} = K_f/\text{process time in minutes}$$

A large K_{ft} indicates fast and efficient processes. Processes having a K_f of 20,000 and a K_{ft} of 500 or greater are preferred in the present invention.

preferred to prepare a stock dispersion which is subsequently mixed into the aqueous solution with agitation.

Because of its high surface area in the dispersed state, the getter readily complexes with the contaminant. The amount of getter used in the process will depend upon factors such as the concentration of the contaminant in the aqueous solution, the desired reduction in contaminant concentration sought, and volume of the aqueous solution being treated. However, it is generally preferred to use an excess of the desired molar reduction of contaminant.

The molar ratio of getter to carrier may vary of from about 10:1 to about 1:10 and will depend upon the dispersibility of the getter. Larger amounts of carrier will be necessary if the getter has poor dispersibility or the getter has extremely high dispersibility (which would inhibit coagulation).

After the contaminated aqueous solution has been contacted with a getter and carrier in dispersed state to form a getter-contaminant material, typically a getter-contaminant complex, the getter-contaminant material may be removed. In contrast to solvent extraction where the getter-contaminant is isolated in a continuous organic solvent phase, the present process comprises forming a discontinuous, usually solid, phase of coalesced particles by simply reducing the dispersibility of carrier. The dispersibility is reduced by reducing the ionizability of the hydrophilic moiety or "polar head" of the carrier by the introduction of an activator or other means of activating by pushing the ionized versus unionized equilibrium towards the unionized state. An activator may be selected with reference to the solubility product (K_{sp}) of the carrier in association with the activator. One advantage of this mechanism and process is that the carrier associated with getter-contaminant material and residual carrier are both made less dispersible. While not wishing to be limited, five basic tech-

TABLE II

RELATIVE PERFORMANCE OF VARIOUS TREATMENTS FOR PROCESSING ONE LITER OF WATER

MATL TYPE	TYPE OF REAGENT	AMOUNT OF MATERIAL REAGENT USED	WEIGHT OF METAL IN WATER		TREATMENT TIME	RELATIVE EFFICIENCY K_f	RELATIVE SPEED EQUAL EFFICIENCY K_{ft}
			INITIAL	FINAL			
Pb	Ion Exchange DP-1	1,000 mg	50 mg	0.05 mg	640 min	9,100	14
Dye	Ion Exchange DP-1	20,000 mg	2 mg	0.20 mg	1 min	5	5
Pb	Magnesium Hydroxide	1,000 mg	10 mg	0.05 mg	100 min	20,000	200
Cd	Solvent Extraction*	401,000 mg	36 mg	1.6 mg	3 min	5.6	1.9
Pb	Example*	150 mg	10 mg	.005 mg	30 min	1,300,000	44,000

*Amberlite DP-1 ion exchange resin available from Rohm and Haas Company, Philadelphia, Pennsylvania.
*Includes weight of solvent.
*Includes weight of salt, carrier and getter used in process

In the present process, a getter compound must be placed in a dispersed state. This ma be achieved by dispersing the getter with a carrier compound directly in the contaminated aqueous solution or by predispersing the getter and carrier in a stock aqueous dispersion which is subsequently contacted with the contaminated aqueous solution. A stock dispersion may be prepared using known dispersing techniques such as using dispersing agents, heating water (preferably above the kraft point of the carrier) or adjusting the pH of the water. The particular method of placing the getter and carrier in a dispersed state will largely depend upon the pH, temperature, and ion composition of the contaminated aqueous solution. For example, in treating an acidic contaminated aqueous solution, it is generally

niques will be discussed:

(1) Adjusting the pH of the aqueous solution. This will depend largely upon the particular carrier used in the process. For example, stearyl phosphate may be made less dispersible by the addition of an acid such as nitric acid and stearyl amine may be made less dispersible by the addition of sodium hydroxide.

(2) Adding divalent or polyvalent metal ions to the aqueous solution. For example, stearyl phosphate may be made less dispersible by the addition of magnesium sulfate to the aqueous solution.

(3) Forming a non-ionizable (water insoluble) salt in the aqueous solution. In the case of stearyl phos-

7

phate, this may be achieved by the addition of silver nitrate.

8

rial is then allowed to settle and/or is filtered from the aqueous solution.

TABLE III

Metal/Toxin	Initial In ppm	Final In ppb	Getter w/Carrier Getter Carrier	Amount In grams	Activator	Amount In grams
Lead	10	18	Cyanex 301* Stearyl phosphate	.05 .05	Ferric Sulfate	0.1
Lead	10	1,800	Cyanex 301 Stearyl phosphate	.05 .05	Sulfuric Acid	0.1
Lead	10	<5	Cyanex 301 Stearyl phosphate	.05 .05	Magnesium Sulfate	0.1
Lead	10	<5	Cyanex 301 Stearyl phosphate	.025 .025	Magnesium Sulfate	0.1
Copper	10	510	Cyanex 301 Stearyl phosphate	.05 .05	Magnesium Sulfate	0.1
Copper	10	610	Cyanex 301 Stearyl phosphate	.05 .05	Ferric sulfate	0.1
Copper	10	310	Cyanex 301 Stearyl phosphate	.05 .05	Sodium sulfate	1.0
Copper	10	<0.5	Cyanex 301 Stearyl phosphate	.05 .05	Sulfuric Acid	0.1
Lead	.3	<0.5	Cyanex 301 Sodium Stearate	.1 .1	Magnesium Sulfate	N/A

*Cyanex 301 is bis (2,4,4-trimethylpentyl) dithiophosphinic acid available from American Cyanamid Company, Wayne, New Jersey.

(4) Adding a salt to reduce dispersibility by the common ion effect. Thus sodium sulfate, potassium sulfate or sodium phosphate may be added to reduce the dispersibility of stearyl phosphate.

(5) Changing the temperature of the aqueous solution. Generally, lowering the temperature decreases dispersibility.

Where an acid, salt or base is added to the aqueous solution to reduce the dispersibility of the carrier, it has been found that the effectiveness of the process may also be affected. Therefore, it is desirable to use acids, salts or bases which are "non-competitive" with the getter-contaminant complex, i.e., do not compete with the contaminant ion to complex with the getter. It is preferred that the added acid, salt or base tends to promote the complexing of the ionized contaminant with residual uncomplexed getter.

In some instances, the addition of an acid, salt or base to reduce dispersibility will not be necessary, since the contaminated aqueous solution may contain, in addition to the contaminant, an acid, salt or base which tends to reduce the dispersibility of the carrier. In treating such contaminated aqueous solutions, it is desirable to first prepare a stock aqueous dispersion of the getter and carrier which is subsequently mixed with the contaminated solution.

The getter-contaminant material in the discontinuous phase may be separated from the aqueous solution using known techniques such as filtering, flocking and/or settling. The getter and carrier may be regenerated using techniques generally known for regenerating contaminant loaded extractants in solvent extraction processing.

The examples set forth in Table III below are illustrative of the process of the present invention. In the examples, the following general procedure was used to treat 1 liter of contaminated aqueous solution. Getter or getter salt and carrier are predispersed in water, usually hot water. It is then added to the contaminated water and is stirred for 15-30 minutes. The activator for reducing dispersibility and about 1 mg of flocking agent are then added together to the aqueous solution and stirred for an additional 30 minutes. The getter-contaminant mate-

I claim:

1. A process for removing a dissolved contaminant from an aqueous solution comprising:
   contacting said aqueous solution with a getter compound selected from the group consisting of bis(2,4,4-trimethylpentyl) dithiophosphinate, diisobutyl dithiophosphinate, di-2-ethyl hexyl dithiophosphinate, di-2-ethylhexyl phosphate, tributy phosphate, bis-diethylthiocarbamoyl disulfide, and bis-dimethyl-thiocarbamoyl disulfide and a nonpolymeric, substantially water-insoluble, reversibly dispersible, soap-like carrier compound having at least one pendant hydrophobic moiety and at least one hydrophilic moiety in a dispersed state to form a getter-contaminant material;
   removing said getter-contaminant material by reducing the dispersibility of said carrier compound to form a discontinuous phase containing said getter-contaminant material and separating said discontinuous phase from said aqueous solution.

2. A process according to claim 1, wherein the carrier compound has at least one covalently bonded pendant n-alkyl radical of 18 to 32 carbon atoms.

3. A process according to claim 1, wherein the carrier compound has at least one covalently bonded pendant stearyl radical.

4. A process according to claim 1, wherein the carrier compound is selected from the group consisting of stearic acid, stearyl phosphate, stearyl amine and mixtures thereof.

5. A process according to claim 1, wherein the getter compound is placed in a dispersed state by dispersing the getter and carrier compound in a stock aqueous dispersion.

6. A process according to claim 5, wherein the getter compound is contacted with the aqueous solution by mixing the stock aqueous dispersion with the aqueous solution.

7. A process according to claim 6, wherein the carrier compound is selected from the group consisting of stearyl phosphate, stearyl amine and stearic acid.

* * * * *

APPENDIX E

LITERATURE ON PERCHLORATE TREATMENT TECHNOLOGIES

by Anderson (1), to prevent swirling from the bottom, and by the of a stabilizing viscosity-increasing component added to the solution this component cannot be added, then the s determination should carried out at several concentrations. Mixing cannot indicate a high value than the true one, thus the highest s obtained (unless extrapolati to zero concentration can be made) should be taken as the best approxima tion to the correct value.

These experiments show the considerable utility of the analytic differential centrifugation method as an accurate tool in the design zonal centrifuge separations. Furthermore, the method may be used w confidence for the determination of s itself, and has a number of adva tages over the commonly used density gradient sedimentation in a sucro gradient in the swinging bucket rotor. Of these, one of the most importa is that a very large number of points may be used to define the depletio curve, whereas in the gradient method a large number of fractions mu be assessed to obtain a single point from which s is extracted. Furthermor droplet sedimentation (7, 8) cannot occur in the method described her

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Reverse Osmosis Separation of Sulfate, Nitrate, and Ammonia from Mining Effluents

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Abstract

Cellulose acetate membranes (osmonics) were characterized in terms of pure water permeability constant (A), solute transport parameter (D_{AM}/K_δ), and mass transfer coefficient (k) with sodium chloride solution as the reference system. Reverse osmosis behavior of sulfate, nitrate, ammonia, and some metal ions was studied as a function of pressure in the range of 100 to 300 psig. Quirke tailings containing nitrate, sulfate, ammonia, and metal ions such as Ca, Mg, Fe, Cu, and Zn were subjected to reverse osmosis at 300 psig, and product water of suitable quality for use in recycle operations was obtained.

INTRODUCTION

Nitrogen in the form of ammonia and ammonium ions is undesirable because it promotes corrosion and stimulates growth of algae, unwanted vegetation, and offensive slimes (1). Nitrogen in the form of nitrates is reported to cause irritation of mucous membranes of the stomach and the bladder. Sulfate in high concentrations is alleged to produce objectionable taste and gastrointestinal irritation and catharsis of the alimentary canal (1). Hence it is necessary to reduce the concentration of nitrate and sulfate from contaminated effluents to acceptable levels.

Reverse osmosis is a good method for the removal of dissolved inorganic and organic species from aqueous solutions, and it is characterized

by low expenditure of energy and simplicity of processing technology. Because high-pressure reverse osmosis requires high capital investment and gives rise to membrane compaction problems, low-pressure reverse osmosis has been the subject of a number of studies (2–11) on the treatment of pollutant-bearing waste effluents in our laboratories. The studies have proved promising in the sense that both valuable metal ion and product water of reasonable quality could be simultaneously recovered for reuse. Hence a systematic study has been undertaken to determine the reverse osmosis separation characteristics of both the individual soluble species present in the mill effluent and the composite solution containing the various pollutants. The results from such studies are reported in this paper together with the levels of some metal ions present in the product water after reverse osmosis treatment.

EXPERIMENTAL

Reverse Osmosis Cell

The conventional stainless steel static cell consisted of a detachable upper part and a lower part. The membrane was placed on a stainless steel porous plate embedded in the lower part of the cell. The lower part of the cell was provided with an outlet through which the membrane-permeated (product) solution was collected at atmospheric pressure. The upper part of the cell contained the feed solution of interest in contact with the membrane under pressure. The two parts of the cell were fitted and sealed with the aid of two concentric rubber O-rings. The effective surface area of the membrane in the cell was 13.4 cm². The required pressure was achieved by compressed nitrogen gas from a gas cylinder. A magnetic stirrer fitted at the top part of the cell, located about 0.64 cm above the membrane, was used to ensure uniform stirring of the feed solution, thereby minimizing concentration polarization effects. The schematic diagram of the whole experimental arrangement is the same as that reported earlier (5). Cellulose acetate membranes obtained from Osmonics Inc. were used in these studies, and characterized in the usual manner (5).

Procedure

All experiments were conducted at laboratory temperature (23–25°C). The membrane was pressurized with pure water at 400 psig for about 2 h before subsequent use in the experiments at operating pressures of 100 to 300 psig. The pure water permeation rate (PWP), the membrane-

permeated product rate (PR) for a given area of the membrane, and the solute separation (f) were determined under present operating conditions. A feed solution containing 1425 mg/L of sodium chloride was used to obtain data on membrane specification and to specify the mass transfer coefficient (k) on the high-pressure side of the membrane. The sodium chloride content of the feed and product solutions was analyzed by conductance measurements. The feed and product solutions containing metal ions Ca, Zn, Fe, Cu, and Mg were analyzed by atomic absorption spectrophotometry at wavelengths of 4227, 2139, 2483, 3248, and 2852 Å, respectively. Sulfate was determined gravimetrically as $BaSO_4$. Ammonia was determined spectrophotometrically using the phenol–hypochlorite method described by Weatherburn (12). Nitrate ion was determined by the phenol–disulfonic acid method of Taras (13). Product rates were corrected with respect to viscosity and temperature (25°C). Because low concentrations were involved, solute separation (f) was calculated using the relationship

$$f = \frac{\text{solute concentration in feed} - \text{solute concentration in product}}{\text{solute concentration in feed}}$$

RESULTS AND DISCUSSION

Membrane and Specifications

The reverse osmosis membranes can be specified in terms of parameters such as the pure water permeability constant (A) and the solute transport parameter (D_{AM}/K_δ) at a particular operating pressure. The solute separation and product rate obtained with a membrane so specified are functions of the mass transfer coefficient (k) on the high-pressure side of the membrane, which is governed by the feed flow rate and the feed concentration used in the experiment. A computer program (14) using experimental data on pure water permeation rate, membrane-permeated product rate, and

TABLE 1

Membrane Specification Data[a]

Film no.	$A \times 10^6$ g mole H_2O (cm⁻² s⁻¹ atm⁻¹)	D_{AM}/K_δ (10⁵ cm/s)	Feed, 1425 mg/L NaCl, $k = 14.29 \times 10^{-4}$ cm/s	
			Solute separation (%)	Product rate (g/h)
1	1.63	5.33	87.40	19.26
1	1.60	5.69	87.00	18.85

[a]Membrane area 13.4 cm²; pressure 300 psig.

solute separation   .esent operating conditions for the aqueous sodium chloride feed solution containing 1425 ppm salt was used in the calcula tion of A, D_{AM}/K_δ, and k. The data presented in Table 1 on the values of A and D_{AM}/K_δ for sodium chloride at 300 psig specify the characteristics of the membrane used in the present studies. The feed flow conditions used in all the experiments done in the present investigation are specified in terms of the corresponding values of k obtained with the reference system of sodium chloride solution containing 1425 ppm of salt. The data presented (Table 1) show the high productivity of the membrane used.

Separation of Salts

The reverse osmosis separation of specific salts such as sodium sulfate, magnesium perchlorate, magnesium chloride, magnesium sulfate, calcium chloride, calcium nitrate, and ammonium nitrate was studied as a function of pressure in the range of 100 to 300 psig. In every case studied the percent separation reaches a maximum at nearly 300 psig (Table 2). Therefore, all further experiments were carried out at a pressure of 300 psig. For all the salts studied, the product rates were found to increase in a linear fashion in going from a pressure of 100 to 300 psig (Table 2). All solutes studied gave a fairly high separation with the exception of ammonium nitrate.

TABLE 2

Separation of Salts

Salt	Concentration (ppm)	Pressure (psig)	PWP (g/h)	Product rate (g/h)	Percent separation
Na$_2$SO$_4$	1034	300	20.9	19.0	93.9
	1034	200	13.7	12.3	94.1
	1034	100	6.6	5.4	93.6
Mg(ClO$_4$)$_2$	830	300	20.3	16.2	94.7
	830	200	13.5	10.2	93.5
	830	100	6.4	3.7	89.8
MgCl$_2$	1010	300	22.5	17.8	87.1
	1010	200	15.1	11.0	86.1
	1010	100	7.1	4.2	78.2
MgSO$_4$	1020	300	22.5	18.6	88.2
	1020	200	14.8	11.8	87.3
	1020	100	7.2	5.1	86.3
CaCl$_2$	820	300	22.1	19.0	89.5
	820	200	14.5	11.8	87.8
	820	100	6.8	5.1	82.9
Ca(NO$_3$)$_2$	910	300	20.6	17.2	94.7
	910	200	14.0	10.8	94.5
	910	100	6.4	4.5	87.9
NH$_4$NO$_3$	3470	300	22.0	19.3	55.0
	3470	200	14.7	12.4	42.9
	3470	100	7.2	6.5	30.3

TABLE 3

Analysis of Quirke Tailings after R.O. Treatment[a]

Constituent	Concentration (ppm)	
	Feed water	Product water
Ca	100.0	5.0
Zn	2.0	0.09
Fe	10.2	0.10
Cu	2.0	0.09
Mg	18.0	1.00
NO$_3$	110.0	47.0
SO$_4$	1170	88.5
NH$_3$	22.6	9.1

[a]Pressure 300 psig; membrane area 13.4 cm^2.

A sample of Quirke tailings effluent was subjected to reverse osmosis treatment at 300 psig, and the product water was analyzed for the metal ions Ca, Zn, Fe, Cu, Mg, and other pollutants such as nitrate, sulfate, and ammonia. The analytical data of the product water from reverse osmosis treatment are given in Table 3. The metal ion concentrations are within acceptable levels as far as environmental limits are concerned.

A comparison of the average concentrations of sulfate and nitrate (1400 ppm SO$_4$ and 120 ppm NO$_3$) in the tailing (15), and the levels found in the product water (88.5 ppm SO$_4$ and 47 ppm NO$_3$) indicate that there is a respective reduction of about 16 and 2.6 times of these species. Further, the sulfate concentration in the product water is also below the average level (142 ppm) (16) found in the Quirke Lake whence the water was drawn for mining operations. However, the nitrate concentration in the permeate is definitely higher than the average level (7.4 ppm) (16) observed in the lake. The product water was subjected to a second stage reverse osmosis treatment. The product water from the second stage reverse osmosis treatment analyzed 19 ppm sulfate, 20 ppm of nitrate, and 4 ppm of ammonia. This sample of product water is satisfactory for recycling purposes.

It can be concluded from these studies that the reverse osmosis treatment of mill effluents of Quirke-type composition can yield product water of suitable quality which can be used in water recycle operations.

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Separation of Individual Cresols from Mixed Cresols

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Abstract

The emphasis of the present work was mainly to develop process conditions for a better yield and purity of m-cresol which is used as a starting material for the production of menthol. Experiments were conducted to isolate m-cresol by a sulfonation-desulfonation method. The various parameters studied included reaction temperature, weight ratio of cresols to sulfuric acid, and reaction time. The best conditions were reaction temperature 80°C, reaction time 5 h, and w/w ratio of cresols to sulfuric acid of 1:1. Under these conditions the conversion of m-cresol to m-cresol sulfonate was 96.5%. After desulfonation the overall recovery of the product m-cresol, based on the amount of m-cresol in the initial crude mixture, was 63%. The purity of the final product was more than 80%. The effects of various impurities (o-, p-cresols, and phenols) are discussed.

The problem of separation of cresol isomers has been studied since the 1920s. o-Cresol can be easily separated by fractional distillation from m- and p-cresols due to the appreciable difference in their boiling points. It is difficult, however, to separate m- and p-cresols from a cresol mixture due to their similar physical and chemical properties. The main use of methylated p-cresol is in the production of an antioxidant (2,6-ditertbutyl p-cresol), whereas m-cresol finds use as the starting material for the production of menthol.

In the past, attempts have been made to separate cresol mixtures. The various methods can be grouped under the headings extractive crystallization (1–5), adductive crystallization, clathration (6, 7), liquid–liquid extraction (8, 9), distillation (10, 11), molecular sieve separation (21), ion exchange techniques (12–14), and chemical methods (15–20). The critical review of all these methods has been reported in the literature (22). In the

Oxidation Chemistry of Energetic Materials in Supercritical Water

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ABSTRACT

The destruction of explosives and rocket fuel components by oxidation in supercritical water is described. The focus is on the major technical issues that must be resolved to make a disposal process practical. These issues include the chemistry of the process and methods for high-throughput processing of the target waste. The destruction efficiencies, the products of reaction contained in the reactor effluents, and methods for achieving high-throughput destruction of several representative explosives and propellant components are reported.

INTRODUCTION

Explosives and pyrotechnics (PEPs) are traditionally disposed of by open burning/open detonation (OB/OD). Regulatory agencies, however, are likely to prohibit OB/OD because of the uncontrolled air emissions and soil contamination. Likewise, controlled incineration carries a liability for air pollution because large quantities of NO_x are produced in the conventional combustion chemistry of PEPs. Soil and ground water have already been contaminated with PEPs through normal operations at manufacturing plants and military bases. Incineration can be used for decontamination of these soils, with the associated liability for air pollution, but few satisfactory and economic methods exist for ground water decontamination. Therefore, a clear need exists for improved disposal and destruction methods.

Previous work has demonstrated the utility of supercritical water oxidation (SCWO) as a waste treatment method. High destruction and removal efficiencies (DREs) have been reported for a broad range of common solid and liquid wastes, including difficult examples such as chlorinated aromatic solvents. [1-3] These same studies have indicated that the major reaction products were water, carbon dioxide, and inorganic salts. The general approach is to mix the waste with an oxidant

(oxygen, air, or hydrogen peroxide) in water at pressures and temperatures above the critical point (374°C and 218 atm). Under these conditions, water is a fluid with densities high enough that reasonable process throughput can be achieved, but its transport properties are like those of a gas, allowing rapid chemical reaction. Supercritical water (SCW) is a unique solvent medium in which oxidation can take place at lower temperatures than incineration, thus limiting the production of NO_x and char. The reaction is entirely enclosed in a pressure vessel at concentrations low enough that the heat of reaction is absorbed by the solvent. As a result, the temperature can be maintained at any desired level (typically in the range 400-650°C). Oxidation occurs rapidly, on the time scale of seconds to minutes, and produces simple products (ideally CO_2, H_2O, and N_2).

A great range of scale appears to be possible for SCWO. Standard pressure-vessel technology can be used in small mobile units or permanent medium-sized surface installations for processing of laboratory or manufacturing wastes. Plants with very large capacities have also been proposed, in which a cylindrical heat exchanger and reaction vessel are placed in the ground by use of oil-field drilling and well-completion technology. A more complete description of the operation of full-scale SCWO units, including materials throughput, mass balances, and equipment design, can be found in several reports. [4]

Compared to other available technologies, SCWO is applicable to a broader range of waste types. It can be used to treat pure organics, contaminated soils and water, sludges, and some inorganics. At present, public concern should not delay obtaining operating permits. The complexity of the technology is comparable to incineration so that with proper engineering and process controls, qualified technicians should be able to be operate and maintain an SCWO unit.

Incineration is an alternative non-specific method for destroying organic materials. Incineration can be operated at a relatively low cost, but requirements for extensive emission controls and difficulties associated with obtaining permits can negate potential advantages. Supercritical water oxidation takes place at a much lower temperature (about 500°C) than incineration. Formation of NO_x from N_2 in air does not occur at low temperature, and the effluent is completely contained and controlled. Supercritical water oxidation can be applied to water containing 20% or less organic waste. By comparison, incineration is not as cost effective at these concentrations. Cost estimates for technologies in the development stage, such as SCWO at full scale, are inherently uncertain and should be considered cautiously. The cost of SCWO of wastes has been estimated in several studies. [3,4] For treating a ton of dry organic material, the costs are estimated to be between $300 and $600 per ton, depending on the size of the SCWO treatment unit. [4] Other methods under development that may apply to explosive wastes include oxidation by hydrogen peroxide and/or ozone with uv radiation, electrochemical oxidation, and oxidation in molten salts. In two-phase systems such as these, concentration gradients across phase boundaries and mass transfer of oxygen limit the rate and extent to which compounds can be completely destroyed. A supercritical fluid is single phase making complete mixing possible; thus, reaction rates are not diffusion limited. A preliminary cost comparison of these oxidation processes prepared by the Energy and Environmental Analysis Group at Los Alamos National Laboratory estimates the costs for the uv processes for contaminated water are 10 to 100 times less per gallon of water than for SCWO. However, these technologies are limited to low [<1000 parts per million (ppm)] organic concentrations. Concentrated wastes would need to be diluted. In addition, these methods usually require special pretreatment of the waste water, thereby increasing costs. In some cases, these methods may destroy the target waste, but often produce harmful by-products a result of incomplete reaction.

This work seeks to examine the behavior of explosives and rocket fuel components, including ammonium perchlorate (AP), cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), hydrazine (N_2H_4), nitroguanidine (NQ), pentaerythritol tetranitrate (PETN), and 2,4,6-trinitrotoluene (TNT) under conditions of SCWO to provide the DREs of the substrates, to determine the optimum conditions for maximizing the DREs, and to ensure safe operation. Products of destruction are identified and measured. Experimental results are evaluated to determine whether the reaction products are environmentally acceptable. Corrosion studies are under way to determine the suitability of various reactor materials. In addition, safety studies are in progress to determine the detonation sensitivity characteristics of PEPs in supercritical water systems.
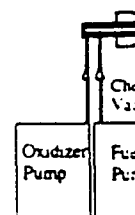
This section describes the reactors used to destroy high-energy materials through SCWO processes, and the analytical methods used to measure product species. The specific experimental conditions under which the destruction measurements were performed will be presented in the results and discussion section.

Bench-scale linear flow reactors have been developed to destroy explosives in supercritical water. A schematic of a linear flow reactor is shown in Figure 1. Solutions of oxidizer and/or explosives are introduced at high pressure into the reactor by constant flow, high-performance liquid chromatography pumps (LDC Analytical, Constametric 3200). The explosives are typically in water at concentrations less than half of their solubility limit or decomposed in water as the result of prior hydrolysis reactions. Check valves are placed in each line to prevent back-streaming in case of pump failure. Fuel and oxidizer are either premixed before being pumped or are introduced separately. In either case, mixing is completed before reaching the heated section of the reactor. The central core of the reactor is heated to a controlled temperature by six heaters in parallel consisting of hollow brass tubes wrapped with MgO_2-insulated nichrome wire. The temperature is maintained by regulating the current through the heating wire with Omega CN9000 series microprocessor temperature controllers. The temperature of each of these heaters can be varied independently, but for all experiments described in this report the temperature of each heated section was kept the same. The temperature is monitored with six K-type (chromel-nickel), sheathed thermocouples in close proximity to the reactor core. A water-cooled heat exchanger at the exit cools the reacted mixture to room temperature. The cooled effluent is passed through a 7-μm filter for removal of any particulate matter before reducing the pressure to ambient with a let-down valve. Gas and liquid effluents at ambient temperature and pressure then enter a gas-liquid separator.
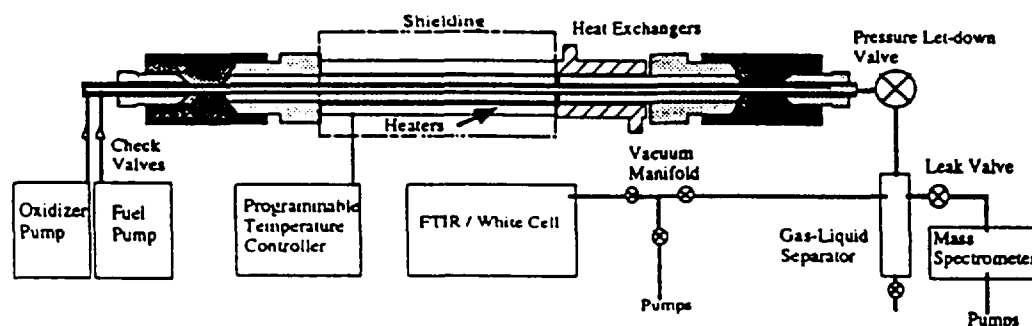
FIGURE 1. Schematic of Linear Flow Reactor with Gas-Liquid Separator, Pumping Manifold, and Gas Analysis Instrumentation.

The high-temperature portion of one of our reactors is constructed out of C-276, a high-nickel alloy chosen because of its known strength and resistance to corrosion at high temperatures. Even so, under some reaction conditions, we have seen considerable corrosion. To overcome this problem, a second reactor was constructed containing a 316 stainless steel sheath with a gold liner. A seal was made with the gold liner by flaring one end of the gold tube and compressing it between tapered high-pressure fittings. The liner is open at the exit of the reactor, creating a static supercritical region between the liner and stainless core. The gold liner protects all high-temperature sections of the reactor. All "taper seal" high-pressure fittings, and most other components obtained from High Pressure Equipment Co., are manufactured from 316 stainless steel and rated to a minimum of 4080 atm. The C-276 reactor core is 64 in. long by 0.083 in. inside diameter (i.d.), and the gold-lined stainless steel reactor is 55 in. × 0.103 in. These dimensions provide a heated volume of 5.7 mL and 7.4 mL, respectively. Using an empirical equation of state for supercritical water [5] we estimate a residence time of 5-150 seconds, depending on flow rate (typically 1-8 grams/min) and temperature (400-600°C) at a pressure of 340 atm.

We have used a variety of analytical approaches in order to quantify residual energetics and products of reaction in the aqueous and gaseous reactor effluents. The gaseous effluent is primarily analyzed using Fourier-Transform Infrared (FTIR) spectrometry. A procedure was developed to quantify the concentration of CO_2 and N_2O (the primary gas-phase products) produced using a 1-m path length cell. Calibration curves for CO_2 and N_2O were obtained by measuring the fraction of infrared light absorbed by a series of known concentrations of CO_2 or N_2O in the range expected to be produced in SCWO reactions. The dependence on concentration of the integrated absorbance of each of the two major CO_2 IR absorptions was nonlinear, exhibiting distinctive saturation behavior over the range of pressures (concentrations) from 0.1 to 10 torr; this was a consequence of the narrow linewidths of the ro-vibrational lines and the limited (0.5 cm^{-1}) resolution of the FTIR. The resulting calibration data were fitted to a saturation function, $y = a(1-e^{-bP})+cP$, where P is the partial pressure of the absorbing gas. This technique enabled us to measure the gas pressure with a relative standard deviation of 3%. A UTI quadrupole mass spectrometer is also used for detection of H_2, N_2, and O_2. Gaseous products are sampled on-line through a leak valve. Calibration of this technique has so far proven difficult, due to constantly changing backgrounds.

Analyses performed on the liquid effluent included metals, total organic carbon (TOC), total inorganic carbon (TIC), inorganic anions and the starting material. Metals (Cr, Ni, Fe, Mo, and Au) are analyzed on a Perkin-Elmer inductively coupled plasma spectrophotometer (ICP) using indium as an internal standard. Total organic carbon (TOC) and total inorganic carbon (TIC) are analyzed using a Rosemount Dohrmann Model DC-190 Carbon Analyzer. Calibrations are performed with each set of samples using different concentrations of standardized potassium acid phthalate solution. Inorganic anions are analyzed with a Dionex 4500i Series Ion Chromatograph using a Dionex IonPac AS4A column with an eluent consisting of 1.5 mM $NaHCO_3$ and 2.2 mM Na_2CO_3. In most cases conductivity detection is used, but a uv/visible detector set at 215 nm is used for low levels of nitrate and nitrite. Trace amounts of TNT, PETN, HMX, NQ, and RDX are analyzed by reverse-phase liquid chromatography on the Dionex 4500i, using a Waters 490E Programmable Multiwavelength Detector that allows for simultaneous, multiwavelength detection. All these compounds are analyzed using a 150 × 2.1 mm i.d. C8 narrow-bore column that is slightly heated for temperature stability.

We developed a colorimetric analytical technique for the quantitative determination of residual hydrazine in SCW reactor effluents. This analytical method is based on Watt and Chrisp. [6] The dihydrochloride of hydrazine is prepared by addition of HCl, and p-dimethylaminobenzaldehyde is then added. The yellow complex formed is analyzed by uv-vis absorption in a Cary 17 spectrophotometer. A calibration curve was acquired for the concentration range of 0.05- to 1.00-ppm hydrazine. The curve was highly linear over this concentration range and yielded a detection limit for hydrazine of 20 parts per billion (ppb).

RESULTS AND DISCUSSION

SCWO Reactions of Energetics Below Solubility Limits

Much of our effort has focused on reactions of solutions having concentrations less than half of their room-temperature solubilities. The destruction efficiencies for the SCWO of five explosive compounds, PETN, HMX, RDX, TNT, and NQ are given in Table 1. These reactions were run at high temperatures (near 600°C) and with a large excess of oxidant.

TABLE 1
Destruction Efficiencies for Energetics Below Water Solubility Limits[a]

Substrate	PETN	HMX	RDX	TNT	NQ
Initial conc. (ppm)	3.8	2.6	35.2	65.5	1700
Destruction efficiency	>0.9825	>0.9900	>0.9992	>0.9998	>0.9999

[a]Conditions: 600°C, 370 atm; excess H_2O_2; 11-s residence time; gold-lined reactor.

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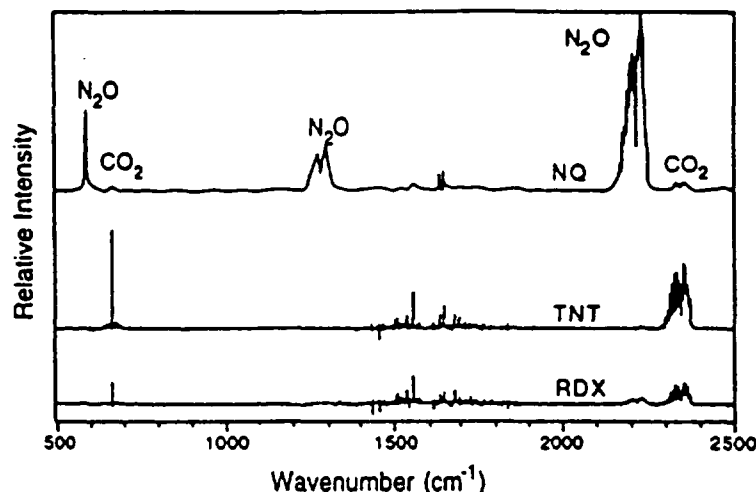
FIGURE 2. FTIR Spectra of the Reaction Products of SCWO of TNT, NQ, and RDX.

The initial concentrations of the explosives were kept low to prevent precipitation and accumulation of explosive material in the feed lines leading to the reactor. Hydrogen peroxide was used as the oxidizer and was mixed with the feedstock containing explosives before the fluids were heated. In all cases the oxidizer was in 30-fold excess of the stoichiometry required to convert the explosive to CO_2, H_2O, and N_2. The experimental conditions for each of these explosives were nearly identical, with pressures of 370 atm, reactor temperatures of 600°C, and residence times of 11 seconds. The reactions were primarily run in the chemically inert gold-lined reactor to minimize the heterogeneous chemistry that might occur at the reactor walls. The only compound for which any reactor-dependent chemistry has been observed is AP. No significant difference in DREs and product formation was observed for reactions of TNT, HMX, and RDX in the C-276 and the gold-lined reactors. We conclude from these observations that reactions with the C-276 and stainless 316 walls must not be significant for these energetic materials. For these "extreme" conditions, the aqueous effluent contained no detectable amounts of explosives. The detection limit of the HPLC/uv-vis analysis ranges from 20 to 50 ppb, depending on the compound. Consequently, the measured destruction efficiencies represent lower limits defined by the low starting concentrations and the detection limits.

Gaseous and liquid effluents from these reactions have been analyzed to determine the products of reaction. Typical FTIR spectra for TNT, NQ and RDX are shown in Figure 2. It is clear from these analyses that the extreme conditions of high temperature and excess oxidant produce only CO_2 and N_2O in the gaseous effluent. Other possible products such as CO, CH_4, NO, and NO_2 are not

TABLE 2

Analysis of Carbon Products in Effluent Streams for SCWO of Energetics[a]

Substrate	$[C]_i$ [b](ppm)	TIC (ppm)[c]	TOC (ppm)[c]	% $C_{aqueous}$	% C_{CO_2}
PETN	2	d	d	d	81
HMX	2	d	d	d	87
TNT	24	0.2	1.7	8	98
RDX	5.7	<0.1	<0.1	<4	98
NQ	195	152	10	83	15

[a]Conditions: 600°C, 370 atm: excess H_2O_2: 11-s residence time: gold-lined reactor; [b]Initial carbon concentration; [c]TIC, Total inorganic carbon, TOC, Total organic carbon; [d]Since starting concentrations of PETN and HMX are ~2-3 ppm, the analyses for TOC and TIC are below detection limits.

detected and are, therefore, below parts per million levels (generally below 0.1% of the starting C and N). Additional products that are likely to be produced in these reactions but which cannot be quantified by FTIR include N_2, O_2 (no infrared active vibrations), and H_2O (swamped by large water background absorption).

The reactor effluents have been analyzed for carbon content and the results are summarized in Table 2. The final two columns list (as a percentage of the initial carbon) the C that is observed in the aqueous effluent (as organic and inorganic C) and as CO_2 in the gaseous effluent. For PETN and HMX, both the TIC and TOC quantities are below detection limits (0.1 ppm). Detectable quantities of organic carbon were found for RDX, TNT, and NQ. Since in all of these cases the substrate is destroyed to levels well below the detection limits of the HPLC analysis (10 ppb), and since no volatile organics were observed in the FTIR analyses, the observed organics must be nonvolatile reaction products such as formate or acetate. For the TNT reactions, greater than 98% of the C was detected as CO_2, with the remainder detected as involatile organics in solution. The only substrate to give significant TIC (carbonate or bicarbonate) quantities was NQ. In this case, 83% of the C was detected as CO_3^{2-} or HCO_3^- while 15% was detected as gaseous CO_2, accounting for most of the C.

Reactor effluents have also been analyzed for nitrogen content and the results are summarized in Table 3. For PETN, HMX, and RDX, some N_2O was observed in the FTIR spectra, but quantitative analysis showed the amounts to be less than 0.5% of the initial N. With excess oxidant, significant amounts of nitrite and nitrate were observed for all substrates except NQ. Most of the detected N from NQ was determined to be N_2O. Trinitrotoluene (TNT) produced the greatest fraction (65%) of NO_x^-. In all cases examined so far, a large fraction of the initial nitrogen remains undetected by our current analytical techniques. We have detected N_2 by mass spectrometry, but not yet quantitatively.

TABLE 3

Analysis of Nitrogen Products in Effluent Streams for SCWO of Energetics[a]

Substrate	PETN	HMX	RDX	TNT	NQ
% NO_3^-	18.7	12.4	10.1	36 6	0.03
% NO_2^-	6.0	5.3	14.1	28.5	0.04
% N_2O	b	b	b	4.0	35

[a]Conditions: 600°C, 370 atm; excess H_2O_2; 11-s residence time; gold-lined reactor. [b]Less than 0.5%.

Effects of temperature and oxidant concentration on SCWO of TNT. An extensive set of experiments has been conducted on TNT to determine the SCWO chemistry as a function of reaction temperature and oxidant concentration. In all cases, the TNT was destroyed to below detection limits of ~10 ppb, yielding a destruction efficiency of greater than 99.98%. The product analysis is summarized in Table 4. The NO_2^- and NO_3^- values are listed as a percentage of the starting nitrogen concentration. Similarly, the TIC and TOC values are listed as a percentage of the starting carbon concentration. The oxidant concentration is expressed as the equivalence ratio, given by the ratio of the stoichiometric concentration to the actual concentration, where the former is defined by the following equation:

$$C_7H_5N_3O_6 + 10.5\ H_2O_2 \rightarrow 7\ CO_2 + 1.5\ N_2 + 13\ H_2O\ .$$
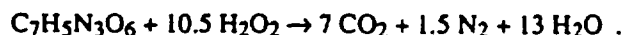
The most efficient conversion of TNT to CO_2, as determined by FTIR analysis of the gas production and by TIC and TOC analysis of the aqueous effluent, occurs at the highest temperature (600°C) and the highest H_2O_2 concentration. These conditions also yielded the highest concentrations of NO_2^- and NO_3^-. This fraction is highly variable, however, depending on the temperature and oxidant concentration. The dependence of NO_x^- formation on oxidant concentration for TNT is illustrated in Figure 3. The fraction of N that occurs as NO_x^- is less than 10% with stoichiometric oxidant concentration. In general, at lower temperatures and lower ratios of H_2O_2:TNT, less NO_2^- and NO_3^- are observed. While these conditions do not compromise the

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TABLE 4

TNT SCWO Products as a Function of Temperature and H_2O_2 Concentration

Temp (°C)	TNT : H_2O_2 equiv. ratio[a]	%NO_2^-	%NO_3^-	%Total NO_x^-	%TIC	%TOC	%Total C
400	1:20	11	30	41	4	18	22
500	1:0	18	0	18	14	28	42
500	1:20	26	51	77	4	11	15
600	1:0	18	0	18	12	34	46
600	1:1	11	6	17	15	0	15
600	1:2	6	6	12	14	0	14
600	1:5	33	38	71	9	0	9
600	1:20	25	49	74	4	0	4

[a]Molar concentration ratio divided by stoichiometric ratio (= 10.5).
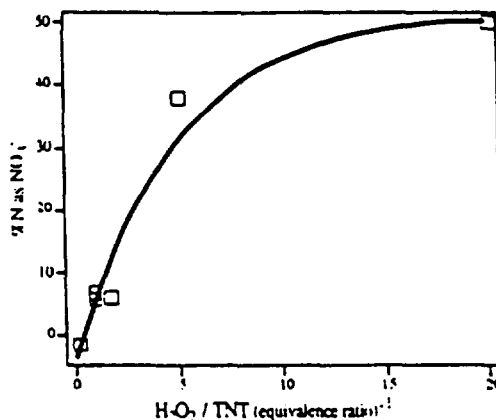
FIGURE 3. Dependence of Nitrate Formation on the Ratio of H_2O_2:TNT.

destruction efficiency of TNT, they tend to leave more carbon in the aqueous effluent. Much of this carbon appears as carbonate, however, which can be removed by lowering the pH. The best conditions for the destruction of TNT and any organic byproducts with minimum NO_2^- and NO_3^- formation appear to be 600°C and a stoichiometric ratio of H_2O_2:TNT.

SCWO Reactions Of Hydrazine. We have made preliminary measurements on the destruction of hydrazine in supercritical water. These measurements were made in the gold-lined reactor with the following conditions: 0.2% (by weight) starting concentration; 600°C; no oxidant; 4 mL/minute flow rate; 370 atm; 11-s residence time. No hydrazine was detected in the effluent acquired under these conditions. Given the starting concentration of 2000 ppm and the detection limit of 20 ppb, this yields a destruction efficiency of greater than 99.999%.

A large quantity of gas was produced in this reaction. However, only NH_3 was detected in the FTIR. We estimate that about 10% of the starting N is converted to NH_3. Since we would have detected NO, NO_2 or H_2NNO in the gaseous effluent, we speculate that the rest of the gas produced is N_2. The liquid effluent was analyzed by HPLC. The only product detected was NH_4^+, probably occurring as NH_4OH. The concentration of NH_4^+ detected represents 12.5% of the starting nitrogen. The nitrate and nitrite concentrations were below detection limits (0.1 ppm).

We have also investigated the reactions of hydrazine with an oxidizer in SCW. We chose the nitrate anion as the oxidizer to simulate reactions of nitrogen tetroxide, since nitric and nitrous acid are produced upon dissolution of N_2O_4 in water. We used a two-fold excess of hydrazine, so that the actual reaction stoichiometry is likely defined as follows:

$$2N_2H_4 + NaNO_3 \rightarrow H_2O + 3/2N_2 + NH_4OH + NaOH \ .$$
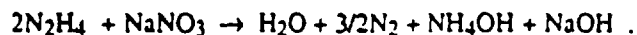
A new reactor was used for this experiment, having the unique feature of a vertical orientation, with the flow against gravity. This feature caused problems since one of the reaction products is NaOH. Sodium hydroxide is molten above 300°C and apparently forms a separate, molten salt phase at the concentrations employed (1000-ppm NaOH). The molten alkaline phase settled out in the bottom of the reactor and severely corroded part of it. Before this occurred, however, we were able to make several runs and determine the chemistry of the hydrazine/nitrate reaction. The first run was at 525°C and 340-atm psi with flow rates of the separate hydrazine and nitrate feed streams of 2 mL/min each. A large quantity of gas was produced in this reaction. We estimate that about 10% of the starting N is converted to N_2O, and expect that much of the rest was converted to N_2. The liquid effluent was analyzed by HPLC, and revealed NH_4^+ in a quantity corresponding to about 9% of the starting nitrogen. The nitrate and nitrite concentrations were below detection limits (0.1 ppm). The reduction of nitrate to nitrogen or nitrous oxide was more than 99.99% complete in this reaction. When the reaction was run at a lower temperature (425°C), the product distribution was essentially the same except that only 99.1% of the nitrate was reduced.

Reactions of Ammonium Perchlorate (AP). The chemistry of AP is different from other explosives and consequently is discussed separately. Because of corrosion problems, most AP experiments were performed in the gold-lined reactor. Some results in the C-276 reactor are included for comparison. Sodium hydroxide was always added to the AP solutions in a 1:1 ratio to ensure a net pH balance. This is particularly important for the gold-lined reactor, where the presence of a high Cl^- ion concentration together with a low pH and highly oxidizing conditions may result in the oxidation of the gold liner to $AuCl_4^-$.

Data for the dependence of destruction efficiencies and reaction products on temperature are summarized in Table 5. The products containing Cl and N are given as a percentage of the initial Cl and N concentration, respectively. At temperatures lower than 400°C, no decomposition of the ammonium perchlorate is observed. Most of the ammonia and all the perchlorate are recovered. The small ammonia loss is most likely due to the evolution of ammonia gas from the feed solution and effluent. The AP begins to react at 450°C and is completely destroyed (99.6%) at 600°C. Almost all the chlorine from the perchlorate appears in the effluent as sodium chloride (NaCl). Although salt solubility decreases in supercritical water, the sodium chloride product remains in solution at low concentrations or temperatures. However, when the concentration and/or temperature are raised, the Cl mass balance is degraded, probably due to precipitation of Cl^- salts in the reactor. We have found that our mass balances improve when the reactor is cooled and flushed between runs and the 'flush' solutions are included in the analysis. With this procedure a burst of Cl^- is generally observed in the first or second flush sample as the reactor is cooled. The liquid effluent also contains a small amount (<2%) of nitrogen as nitrite (NO_2^-) and nitrate (NO_3^-). The mass spectra indicated that both nitrous oxide (N_2O) and oxygen (O_2) are produced. The amount of N_2O produced was quantified by FTIR and appears to increase with increasing temperature and AP concentration. Most of the N was not detected (for the best case, 600°C, only 25% is detected) and likely occurs as N_2. The FTIR and mass spectrometric analyses of the gaseous effluent did not detect the presence of chlorine (Cl_2), nitrosyl chloride (NOCl), or nitrogen dioxide (NO_2).

TABLE 5

AP SCWO Products as a Function of Temperature[a]

T (°C)	% ClO$_4^-$	% Cl$^-$	% NO$_2^-$	% NO$_3^-$	% N$_2$O	%NH$_4^+$
400	100	0.0	0.3	0.0	0.0	95.0
450	95.5	6.9	0.8	0.3	1.3	85
500	46.0	16.0	0.0	2.0	13.6	40.0
550	3.5	17.0	0.0	2.0	23.1	0.0
600	0.4	5.0	0.2	0.2	23.3	0.0

[a] Conditions: 0.1 M AP; equimolar NaOH; residence time varied from 11 to 52 s (600 - 400°C); flush between runs not analyzed; gold-lined reactor.

Previous studies of the thermal decomposition of solid ammonium perchlorate show that a variety of products are possible. [7] Below 300°C, the equation

$$4 NH_4ClO_4 \rightarrow 2 Cl_2 + 3 O_2 + 8 H_2O + 2 N_2O .$$
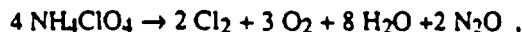
represents the majority of the products. At higher temperatures nitric oxide (NO) is produced. Between 350°C and 450°C gas analysis of the products of thermal decomposition gives

$$10 NH_4ClO_4 \rightarrow 2.5 Cl_2 + 6.4 O_2 + 18.8 H_2O + 2 N_2O + 2.5 NOCl$$
$$+ HClO_4 + 1.5 HCl + 1.75 N_2 .$$
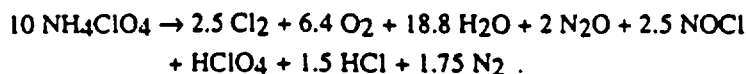
Thus, the decomposition of AP in supercritical water avoids the formation of the hazardous products (Cl_2, NOCl) formed in thermal decomposition.

Above 450°C, ammonium perchlorate detonates. The possibility of explosive energy release was investigated. Concentrated solutions of ammonium perchlorate (1.0 M, 122 g/L) were rapidly heated to temperatures over 600°C at pressures near 340 atm in a small batch reactor. Neither pressure nor temperature transients indicative of rapid energy release was observed. These results indicate SCWO is, therefore, more controlled, i.e., safer than thermal decomposition.

Reactor Corrosion. Corrosion of metals and alloys at high temperature and pressure is an important issue for applying supercritical fluid technology to the treatment of hazardous wastes. Corrosion may in fact be a cost-limiting factor for scale-up to large SCWO facilities. Corrosion is inherently electrochemical in nature, so an understanding of the oxidation-reduction reaction chemistry in supercritical environments is essential for eventual control of these corrosion processes. The most corrosive substance we have run to date is ammonium perchlorate. When running AP in the C-276 alloy reactor corrosion was evidenced by the dark-colored effluent. Analyses are presented in Table 6. Most corrosion products formed insoluble salts in supercritical water. While it was generally possible to flush the insoluble salts out of the reactor during the cool-down phase, the reactor eventually plugged and could not be reopened. The gold-lined reactor was built to avoid these corrosion problems.

TABLE 6

Corrosion Products for SCWO of Ammonium Perchlorate

Reactor material	Au (ppm)	Cr (ppm)	Fe (ppm)	Mo (ppm)	Ni (ppm)
C-276 alloy	---	130.00	---	54.00	39.00
Gold-lined Stainless steel (acidic)	1622.00	3.36	65.38	---	55.04
Gold-lined Stainless steel (alkaline)	0	0.99	0.99	---	3.73

We have run AP in the gold-lined reactor in both alkaline and acidic solutions. Significant corrosion is observed in acidic solutions of AP. At low pH, the oxidation of gold, $Au^0 \rightarrow Au^{+3} + 3e^-$ is activated. The oxidant could be NO_3^- produced in the decomposition of AP or the perchlorate itself. The gold complexes with chloride ion and is dissolved into solution as $AuCl_4^-$. These reactions are analogous to the well known dissolution of gold in aqua regia. By raising the pH, this corrosion pathway is blocked, as shown in Table 6. What little corrosion we do see probably occurred on exposed, hot stainless steel portions of the reactor. In contrast with AP, other explosives have exhibited very little corrosivity.

Increasing Process Throughput

While the previously described experiments are necessary to determine the SCWO chemistry of explosives and propellants, a practical process could not be developed based on introducing many of

these materials below their solubility limits in water. Much greater throughput is required to make the process economically feasible. Calculations based on heats of combustion suggest that aqueous solutions containing 8-12 weight percent explosives are required to produce self-sustaining operating conditions. The primary difficulty in achieving these conditions is the very low solubility of explosives in liquid water. We have examined three potential approaches to this problem.

Co-solvent. The first approach is to predissolve the explosive in an organic co-solvent. A series of experiments were conducted in which a solution of 1% HMX in methyl ethyl ketone (MEK) was injected into water in varying ratios under supercritical conditions. No oxidant was added in these experiments. Temperatures at the injector were varied from 100°C to 400°C, while the pressure was maintained between 350 and 375 atm. For most experiments the water flow rate, 3 mL/minute, was kept about 7.5 times greater than the HMX/MEK flow rate, 0.4 mL/minute. For a few experiments the flow rates of the two solutions were set equal at 3.0 mL/minute. These injection rates yield high concentrations of HMX ranging from 0.1% to 0.5%. Much higher concentrations could be achieved by using a higher initial concentration of HMX in MEK. The injection and subsequent mixing were observed through an optical window using a TV camera and magnifying optics. Under these conditions no solid phase of HMX (due to precipitation of insoluble material) was observed.

For these operating conditions, less than 10% of the MEK was destroyed. A large number of organic products were observed in the HPLC analyses, most likely from the thermal decomposition of the MEK. The identity of these products has not been determined. The HMX was completely destroyed for all concentrations employed. The highest HMX concentration employed was 5000 ppm, yielding a detection-limited destruction efficiency of 99.9996%. The effluent contained low concentrations of nitrite (0.3 to 6 ppm) and nitrate (0.1 to 0.6 ppm). Less than 0.5% of the nitrogen in the HMX is converted to NO_x^-. This result differs from experiments in which HMX is the only organic present in solution. The high concentration of MEK and low level of oxidizer produces a smaller percentage of nitrogen as NO_x^-.

Dissolving HMX in MEK is convenient for introducing high concentrations of HMX into the reactor. However, this approach produces significant quantities of MEK decomposition products. Although thermal decomposition of the MEK is relatively low at temperatures at which most of the HMX decomposes, these products not only interfere significantly with the analysis of the HMX reaction products, but are themselves likely to be undesirable waste. It would be possible to separate the remaining MEK for reuse and to destroy the MEK decomposition products in a second SCWO step. The extra energy and oxidant required for these steps are likely to be significant. This disadvantage could be overcome by using a co-solvent that is inert to oxidation, such as supercritical CO_2. We are currently exploring the solubility of energetic materials in supercritical CO_2 and the effect on the chemistry of injection of large quantities of CO_2 into the SCWO phase.

Slurry Feeding. One of the simplest methods to feed high concentrations of explosives into a supercritical water reactor is in the form of a slurry of small particles (<100 μm) in water. This method presents potential safety hazards because it requires mechanical pumping and heating of solid explosive particles entrained in water. An explosion could occur if sufficient material collects or settles in the reactor feed tubes. In addition, the operation of the SCWO reactor could be difficult to control if the rate of reaction of the explosive depends strongly on particle size or morphology. To help evaluate the hazards associated with processing slurries of explosives, we examined the behavior of small particles in high temperature water.

Slurries of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) were chosen for preliminary studies because of its inertness and high deflagration temperature ($T_d = 384°C$), which is above the critical temperature of water. Quantitative measurements of the temperature and pressure changes resulting from reactions of slurries as they were heated were made in a batch reactor. The reactor volume was adjusted to 200 μL to permit the use of small quantities of material. Milligrams of explosives were added to 100 μL of water to make a slurry of 5 to 20% explosive by weight. The balance of the reactor volume was air. The pressure and temperature of the reactor were recorded at 1-s intervals on a computer as the reactor temperature was increased in a controlled ramp. The pressure rise due to reaction of the explosive was determined by obtaining a baseline pressure rise using an equal quantity of water with no explosive. The pressure difference gives a measure of both the extent and rate of reaction of the explosive. Figure 4 shows results for the behavior of TATB as it is heated. It is interesting to note that while the deflagration temperature of TATB is 384°C, it begins to react at significantly lower temperatures (300-330°C). For quantities of TATB less than 10 mg (10% by

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FIGURE 4. F

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weight), the reaction is generally slow, requiring more than 30 seconds to reach a constant pressure (complete reaction). Quantities greater than 13 mg always yielded a sudden pressure rise, which occurred in less than our 1-s time resolution. One exception was a run with 8 mg of TATB which also showed a sudden pressure rise. This behavior may depend on the degree of dispersion of the solid in the water. The slurry was not stirred or agitated and some settling or clumping of the "wet" TATB may have occurred, leading to self-heating and faster reaction.
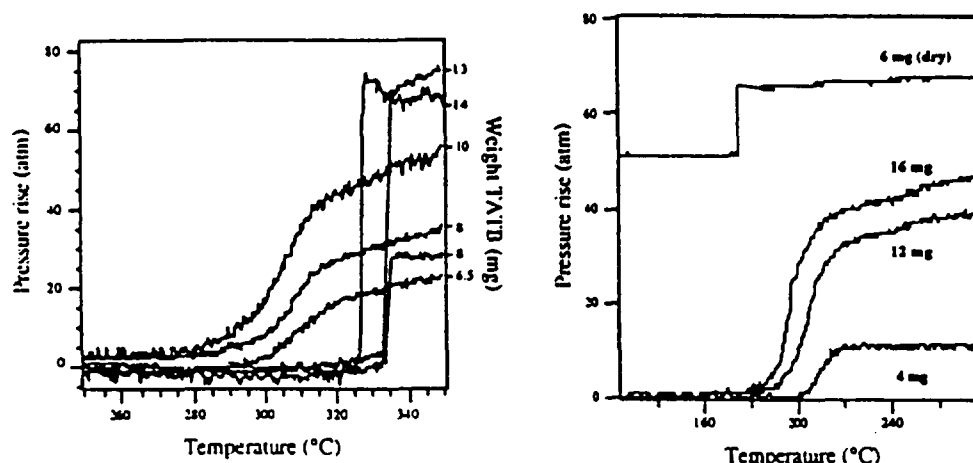
FIGURE 4. Pressure rises observed due to reactions of TATB (left) and DBP (right) slurries in water as a function of temperature and starting concentration. Background pressure rise due to water has been subtracted.

In contrast, similar experiments performed with a double-base propellant (DBP, nitroglycerin/nitrocellulose), shown in Figure 4, show no unpredictable behavior. Reactions were performed with slurries composed of up to 16% by weight of the DBP. Slow pressure releases (reactions) were observed in every case; however, further studies are required to ensure that this is generally true. A run made without water is also shown to demonstrate the rapid reaction (deflagration) that occurs in the pure material.

Base Hydrolysis. A promising approach appears to be pretreatment of the energetic materials to increase their solubility in water. Our effort has focused on degradation of the explosive via base-catalyzed hydrolysis at elevated temperatures. The hydrolysis was carried out using sodium hydroxide equimolar with the explosive in water at elevated temperatures between 75 and 100°C. These reactions produce water-soluble products that are further processed in SCW to achieve complete destruction of the energetic material and its hydrolysis by-products. This approach has been successfully demonstrated for NQ, TNT, HMX, and RDX. Because solutions at high concentration may be processed, very high destruction efficiencies of the starting materials have been measured. In addition, the final products of the combined hydrolysis/SCWO process are very similar to those obtained with SCWO alone.

TABLE 7

Hydrolysis/SCWO of TNT

Substrate	Initial Concentration ppm (%†)	Hydrolysis ppm (%†)	SCWO ppm (%†)
TNT	14000	<2 (<0.02)	<0.05 (<0.0005)
TOC	5181	3380 (65)	<0.2 (<0.004)
TIC	0	1080 (21)	10 (0.2)
N as NO₂⁻	0	784 (30)	8.5 (0.3)
N as NO₃⁻	0	1 (0.04)	20 (0.8)

†Percent of initial substrate concentration.

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TABLE 8
Hydrolysis/SCWO of HMX

Substrate	Initial Concentration ppm (%)[†]	Hydrolysis ppm (%)[†]	SCWO ppm (%)[†]
HMX	7000	22.5 (0.3)	<0.05 (<0.001)
TOC	1123	1026 (91)	0.7 (0.06)
TIC	0	<0.5 (<0.05)	0.2 (0.02)
N as NO_2^-	0	184 (7)	0.09 (0.03)
N as NO_3^-	0	80 (3)	30 (1.1)

[†]Percent of initial substrate concentration.

Results for the combined hydrolysis and SCWO of TNT and HMX are summarized in Tables 7 and 8. It is clear from these results that while the hydrolysis reactions effectively destroy most of the starting explosive, a substantial fraction of the carbon remains in solution as organic material. While much of the N is not accounted for following hydrolysis, qualitative analyses of the off-gases indicate formation of only two N-containing products, N_2 and N_2O. The rest occurs primarily as nitrite. The hydrolyzed solutions were processed in supercritical water using the following conditions: gold-lined reactor, 600°C, 11-s residence time, 350 atm, and excess H_2O_2. Under these conditions, the organic carbon is completely converted to CO_2. Approximately 1% of the starting N is converted to nitrate, corresponding to tens of ppm in the effluent. Future experiments will focus on optimizing the SCWO step to minimize nitrate production.

CONCLUSIONS

In general, the chemistry of oxidation of energetic materials in supercritical water is very similar to that found previously for other classes of organics. We have established conditions for which the hydrocarbon elements of all the energetic compounds investigated thus far are completely oxidized to CO_2 and H_2O. The temperature, residence time, and oxidant concentration necessary to achieve complete oxidation depend on the nature of the energetic material. Our results indicate that complete oxidation to CO_2 and H_2O is always achievable using excess oxidant and operating the reactor at 600°C (11-s residence time). Reasonable carbon balances are obtained for all the energetic materials investigated (PETN, HMX, TNT, RDX, and NQ). Most of the carbon is detected as CO_2, with some small fraction remaining in solution as inorganic carbon (CO_3^{2-} or HCO_3^-). The exception is NQ, which produces large quantities of inorganic carbon. The conditions that produce these results were deliberately "extreme" to ensure complete oxidation. We have not adequately explored the dependence of the chemistry on oxidant concentration and temperature to determine optimum conditions. Minimization of oxidant concentration is particularly important since the oxidant represents a significant fraction of the process cost and if present in excess may enhance corrosion or cause the formation of undesirable products. Furthermore, we have very little data for one variable, the reactor residence time. Less "extreme" conditions (e.g., lower temperatures and stoichiometric oxidant) may be sufficient to achieve complete oxidation in longer residence times. Without added oxidant, products of incomplete oxidation were observed, including CO and CH_4. These products are highly undesirable because of their toxicity and/or flammability. Therefore, a necessary part of process control is on-line analysis for the detection of products of incomplete oxidation in the event of loss of oxidant or other such failure. The criteria necessary for on-line analysis are parts-per-million sensitivity, specificity for multiple components of complex mixtures and rapid response (seconds). The techniques of FTIR and mass spectrometry would probably be suitable.

The nitrogen chemistry of energetics is considerably more complicated than the carbon chemistry, varying widely depending on the nature of the starting material. The nitrogen is always distributed among a group of products, N_2, N_2O, NO_2^-, and NO_3^-, having formal oxidation states of N varying from 3- to 6+. Quantitative data have been obtained for all products except N_2. The latter is implicated as the major N product in many of the reactions by elimination of other possible products. Qualitative data (mass spectroscopy and gas chromatography) indicate N_2 production in

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the case of NM, NQ, and TNT. No obvious correlation exists between the nitrogen content or the type of nitrogen groups ($-NO_2$ or $-NH_2$) of a particular energetic material and the distribution of nitrogen products (N_2, N_2O, NO_2^-, and NO_3^-). It is possible, however, to vary the distribution of products in the different oxidation states by varying the temperature and the oxidant concentration. The clearest example of this tunability is NO_x^- production in the reactions of TNT. When a large excess of oxidant is employed at 600°C, a significant fraction of the initial N (74%) is converted to NO_x^-. This fraction is much less (12%) for a small (5-fold) excess of oxidant and yet complete oxidation of the carbon still occurs. The same trend is observed for the oxidation of RDX with excess H_2O_2 (10% NO_3^-) and with oxygen balance (no NO_3^-). These results indicate that significant control over the oxidation chemistry is possible through the precise tuning of reaction parameters.

The destruction chemistry of AP in SCWO is unique among the energetic materials since AP has no carbon and is a strong oxidant. The chemistry is best described by the following equation:

$$NH_4ClO_4 + NaOH \rightarrow NaCl + 2.5\ H_2O + 0.4\ N_2 + 0.1\ N_2O + 1.2\ O_2 .$$
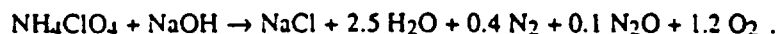
Conditions have been determined for which 99.6% of the ClO_4^- is destroyed. The Cl is converted to Cl^-, formally reduced from 7^+ to 1^-, and excess oxygen is produced in the reaction. Further evidence for the highly oxidizing nature of this reaction is provided by the strong oxidative corrosion of the C-276 and 316 stainless steel reactors. The addition of reducing equivalents, in the form of a fuel such as a hydrocarbon, may improve the destruction of AP as well as reduce the extent of corrosion. The nitrogen is distributed between N_2 and N_2O, with no formation of higher oxides or NO_x^-. In contrast to thermal decomposition of solid AP, no harmful products such as Cl_2 or NOCl are formed in the SCWO reactions.

A critical issue for practical application of an SCWO process to the treatment of energetic materials is reactor wear caused by corrosion. Corrosion of the C-276 reactor by most of the energetic materials does not appear to be a problem, with the exception of AP, which caused severe corrosion of the C-276 and 316 stainless reactors. For laboratory scale reactors, the use of a gold liner in the SCW region reduces corrosion to acceptable levels.

The three methods investigated for increasing process throughput all hold promise as practical approaches to a disposal process. The simplest technique is slurry pumping, which requires fewer steps, a smaller capital investment and no added chemicals. If the safety issues associated with slurries can be resolved, this may emerge as the method of choice.

ACKNOWLEDGMENTS

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Fixed-Bed Photocatalysts for Solar Decontamination of Water

Yin Zhang, John C. Crittenden,* David W. Hand, and David L. Perram

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A solar decontamination process for water was developed using TiO$_2$ photocatalysts supported on silica-based material. The supported catalysts were systematically optimized with respect to catalyst type, catalyst dosage, silica-based support material, particle size, catalyst/support bonding, and calcination temperature. The optimized supported catalysts outperformed an optimized slurry catalyst under identical operational conditions and had a reaction rate four times that of the slurry catalyst. Trichloroethylene (TCE) as a model compound was also used to investigate the impact of solar irradiance, influent concentration, pH value, and hydraulic loading. Supported photocatalysts displayed high light efficiencies over a wide range of weather conditions, an apparent quantum yield of 40% was obtained in a rainy late-afternoon experiment. The complete mineralization of TCE was achieved, and in addition, background natural organic matter (BNOM) in a local surface water did not interfere with the degradation significantly.

Introduction

Photocatalysis and other advanced oxidation processes (AOPs) may play an important role in dealing with today's challenging demand for new drinking water treatment technologies. A wide spectrum of organic contaminants may be photocatalytically degraded into nontoxic forms—simple mineral acids, carbon dioxide, and water. These include the compounds not amendable to treatment using conventional methods such as carbon/resin adsorption and air stripping (1-3).

Ultraviolet (UV) illumination of a semiconductor photocatalyst in an aqueous solution establishes a redox environment capable of degrading organic chemicals. As in other AOPs, hydroxyl radicals (OH) are thought to be the primary oxidants responsible for the degradation of organic contaminants in photocatalysis. Direct and other indirect reactions of organic molecules with valence band holes (h$^+_{vb}$) and conduction band electrons (e$^-_{cb}$) may also contribute to the disappearance of organic compounds (4, 5). TiO$_2$ (anatase) has an energy bandgap of 3.2 eV and can be activated by UV illumination with a wavelength up to 387.5 nm. At the ground level, solar irradiation starts at a wavelength of about 300 nm. Therefore, the 300-387.5-nm portion of the solar irradiation may be used for photocatalysis involving anatase (TiO$_2$). This UV portion is a few percent of the total solar spectrum that comes with direct and diffused components.

Chlorinated alkenes and alkanes including TCE have been degraded mainly by using UV illuminated TiO$_2$ slurries (6-11). A degradation intermediate was detected and identified, and complete mineralization of TCE to HCl and CO$_2$ was eventually achieved in a couple of cases (6,8). Glaze and co-workers (10) found intermediates such as dichloroacetaldehyde, dichloroacetic acid, and two other trace compounds. They proposed a dual mechanism in which TCE is mineralized by a reaction scheme initiated by the OH radical while traces of trichlorinated acetic acid intermediates may also be formed and a parallel reaction scheme in which dichlorinated intermediates are formed on the reduction side of the TiO$_2$ h$^+_{vb}$ - e$^-_{cb}$ couple. Pruden and Ollis (6) used a Langmuir-Hinshelwood form rate expression to examine the TCE degradation kinetics. By including an intermediate, they found that the rate expression satisfactorily represented the disappearance of both TCE and the intermediate and the inhibitory influence of the product HCl.

In the summer of 1991, a solar detoxification system was tested at a Superfund site where groundwater was contaminated principally by TCE (11). The test used a concentrating solar collector with an effective concentration ratio of approximately 20. For a typical influent of 80 µg/L, nearly 90% conversion was achieved in a TiO$_2$ slurry with a 10-min residence time. After adjusting the pH value from 7 to 5.6 to suppress bicarbonate (HCO$_3^-$), a known OH radical scavenger, the effluent level was lowered to less than 0.5 µg/L.

The major objectives of this research were to identify optimal photocatalyst/support options and to explore the use of solar irradiation in photocatalysis for the degradation of organic contaminants (TCE) in water. Fixing TiO$_2$ on silica-based supports not only avoided the effluent slurry separation but also enhanced degradation kinetics and light efficiency. Using solar irradiation as the UV source under a variety of weather conditions throughout the year, this fixed-bed photocatalytic process has many potential applications. Optimal catalyst/support options were identified by considering: (a) type of photocatalyst, (b) support material, (c) catalyst dosage on the support, (d) support particle size, (e) method of attaching the photocatalyst onto the support, and (f) calcination temperature. The following factors were examined by using the optimized catalyst/support options: (a) solar irradiance and weather conditions, (b) time of year, (c) hydraulic loading, (d) influent TCE concentration, (e) dissolved oxygen (DO), (f) pH, and (g) BNOM.

In a previous study, Suri et al. (12) showed that the selection of a suitable catalyst depends on target compounds. In a slurry batch reactor, they found the best catalyst for TCE was 1 wt % platinum (Pt) surface-modified TiO$_2$. The Pt on TiO$_2$ surface is thought to enhance surface charge separation and in turn increase the photoactivity of the catalyst. In this study, the 1 wt % Pt surface modified TiO$_2$—later referred as platinized TiO$_2$—was fixed onto various silica-based supports and tested in continuous flow reactors. For comparison, some experimental runs also used non-platinized TiO$_2$.

Materials and Methods

Reagent-grade (99.9+%) TiO$_2$ (Lot No. 00108TV) was obtained from Aldrich Chemical Co. (Milwaukee, WI). X-ray diffraction revealed that more than 99% of its crystalline portion is anatase. The platinized TiO$_2$ was prepared by photoreducing Pt on TiO$_2$ surface from hydrogen hexachloroplatinate(IV) hydrate (99.995%, Aldrich Chemical), following a method similar to the one described by Kraeutler and Bard (13).

Table 1. Physical Properties of Photocatalyst Support Options

support	sizes tested (mesh × mesh)	light transmission and/or other properties
support A (Ottawa sand)	20 × 30, 30 × 40, 40 × 50, 50 × 60, 60 × 70	light transmission for 2-mm thickness and 40 × 50 mesh size, 7%;[a] particle density, 2.69 g/cm^{3}; bed porosity, 0.40 (size 20 × 30)
support B (silica gel)	35 × 40, 40 × 50, 50 × 60, 60 × 70, 70 × 80, 35 × 60	light transmission for 2-mm thickness and 35 × 60 mesh size, 45%[a] (with 1 wt % Pt-TiO$_2$, 25%); particle density, 0.98 g/cm^{3}; bed porosity, 0.39 (size 35 × 60)
support C (glass beads)	25 mesh size	light transmission for 2-mm thickness, 11%;[a] particle density, 2.94 g/cm^{3}; bed porosity, 0.44
support D (glass fiber mesh)	N/A[b]	light transmission for 4-fold, 17%[a]
support E (glass wool fiber)	N/A[b]	large specific area

[a] UV (300–400-nm, solar irradiation) transmittance. [b] Not applicable.

After reducing the number of support options based on mass transfer considerations and UV transmission measurements, the five silica-based materials, as described in Table 1, were evaluated as photocatalyst supports with TCE degradation. Support A is Ottawa sand (Ottawa, IL); support B is Davisil silica gel from Aldrich; support C is 1-mm diameter glass beads from B. Braun Biotech Inc. (Allentown, PA); support D is TiO$_2$-impregnated fiberglass mesh obtained from Nutech Environmental (London, Ontario, Canada); and support E is G-8389 glass wool fiber from Sigma Chemical Co. (St. Louis, MO). Supported catalysts—except the support D option—were prepared by mixing a concentrated TiO$_2$ slurry with the silica-based support material and calcining the dried mixture in air. For example, to make 200 g of supported catalyst (on silica gel) with 1 wt % catalyst loading, the concentrated slurry was made by sonicating a blend of 2 g of catalyst and 200 mL of water with a Dynatech (Chantilly, VA) Model 300 sonic dismembrator for 15 min. The slurry was mixed with 200 g of silica gel and dried at ambient temperature in air. The catalyst/support mixture was then calcined in air at a temperature of 600 °C for 24 h. Beside this example, the optimized temperature of 600 °C was also used (unless otherwise stated) in most cases of this study. The loss of catalyst in the preparation process was minimal, and the catalyst dosages reported are the starting catalyst weight percentages of their supports.

The solar photocatalytic reactor was constructed in a series of four 25-cm-long plastic tubes with 1/4-in. i.d. and 3/8-in. o.d. (made from M-7 plastic, a patented material, American Energy Technologies, Green Cove Springs, FL). A 1/8-in. thick M-7 plate has an average of 80% transmittance of UV light in the 300–400-nm wavelength range. This value of transmittance was found no decrease in a 5-year test. As shown in Figure 1, five ports were available along the reactor, this enabled the sampling at the influent and after 25, 50, 75, and 100 cm of reactor length. Up to 16 reactors, 15 cm apart from each other as shown in Figure 2, could be mounted in front of a flat metal plate reflector, which reflected about 60% of the UV light. The distance from the photoreactors to the reflector was 8 cm. Considering the location and duration of the test, the plate was tilted about 45° toward the sun to maximize the solar irradiation. These reactors were operated in parallel so various catalyst/support options could be compared to one another under identical conditions (solar irradiance, temperature, influent concentration, etc.).

An EG&G Gamma Scientific (San Diego, CA) Model GS 3100 spectroradiometer was used to measure solar irradiance. A miniature cosine receptor was connected to the spectroradiometer by using a fiber optic probe. The light measurement system was calibrated with an EG&G
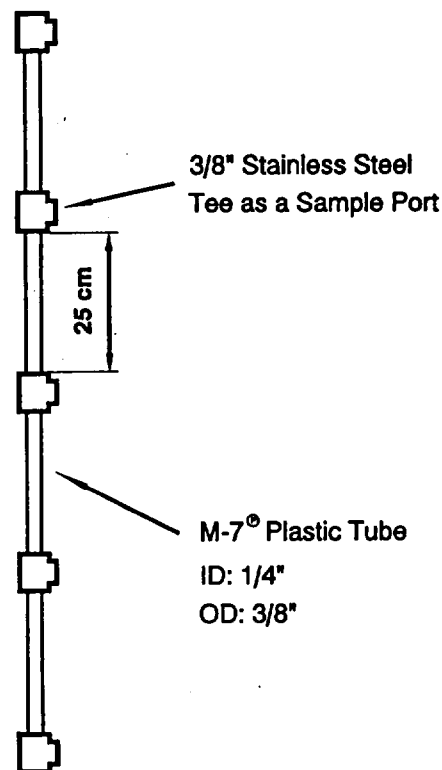
Figure 1. Detailed schematic of the solar photoreactor.

3/8" Stainless Steel Tee as a Sample Port

25 cm

M-7® Plastic Tube
ID: 1/4"
OD: 3/8"
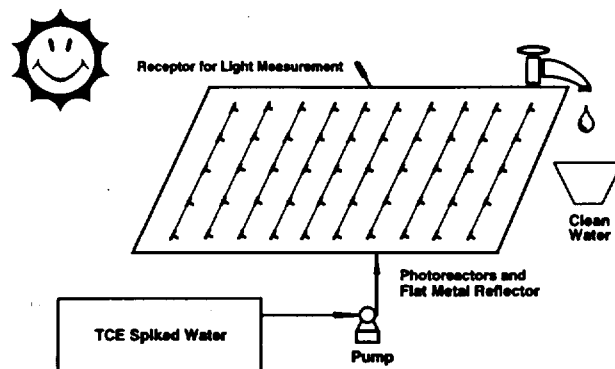
Figure 2. Schematic of the experimental setup used for screening catalyst/reactor options.

Gamma Scientific Model GS-5150 deuterium lamp in a wavelength range of 250–400 nm. According to the manufacturer, the GS-5150 lamp together with the GS-5120 power supply provides a calibration system with accuracy traceable to the National Institute of Standards and Technology (NIST—formerly National Bureau of Standards, NBS). The receptor was mounted at the top of the reflector plate and could rotate to trace daytime sun movement. All light measurements were made by

recording solar irradiance in the wavelength range of 300–387.5 nm with the receptor directly pointing to the sun. All experiments were conducted under nonblocked sunlight, unless otherwise specified.

Slurries of platinized TiO₂ were passed through some of the reactor tubes to compare to catalyst/support options. A slurry was diluted from a concentrated one which was made by using the same method described earlier for the preparation of the supported catalysts. Periodic manual agitation was used to keep TiO_2 particles in suspension.

TCE concentrations were analyzed with direct aqueous injection (Supelco GC Bulletin 816A, Supelco, Inc., Houston, TX) by using a Hewlett-Packard (HP; Palo Alto, CA) 5880A gas chromatography (GC). The GC was equipped with a 2.4 m × 2 mm glass 3% carbowax 1500 on carbopack B (80 × 100 mesh) column and a Ni^{63} electron capture detector. The standards were prepared from pure reagents following the modified EPA standard method 601. A minimum of eight standard concentrations was run for each set of samples. Concentrations of nonpurgeable organic carbon (NPOC) were determined using a Dorhman DC-180 (Santa Clara, CA) organic carbon analyzer. The NPOC analyzer was calibrated with potassium hydrogen phthalate (KHP, as NPOC concentration of 4 mg/L). The detection limit of the analyzer was determined as 0.1 mg/L. Chloride ion concentrations were measured using Dionex (Sunnyvale, CA) Model 12 ion chromatography (IC). A Dionex HPIC AS-3 analytical column was used along with a guard AG-3 column. The eluent used was 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3, and the regenerant was 0.025 N H_2SO_4. The standards were made by using reagent-grade potassium chloride (KCl) following EPA standard method 300.0, and five calibration standards were run for each set of samples. Dissolved oxygen (DO) was measured using a YSI (Yellow Springs, OH) Model 54A oxygen meter, and pH was determined using an Orion (Cambridge, MA) Model 501 digital ionalyzer.

Reagent-grade TCE (99+%) was obtained from Aldrich. The water used in all the test runs, except tests on a local surface water, was distilled and further purified by a Milli-Q purification system (Millipore Corp., Bedford, MA). The DO in the Milli-Q water was saturated, and the initial pH value was about 6.5. The surface water was obtained from Portage Lake, Houghton, MI, and the NPOC concentration was about 2 mg/L. The initial DO and pH of the surface water were 9.0 mg/L and 7.4, respectively. A saturated TCE aqueous solution was used to make various influent concentrations.

Results and Discussions

According to Ollis et al. (2) and Link (14), the major obstacle to the implementation of photocatalysis is the engineering of cost-effective reactors. Reactors that employ a catalyst suspended in slurry and a catalyst fixed on support are two major reactor options. As far as continuous flow operation is concerned, a number of investigators have reported the degradation of various organic compounds with either slurry (1, 7, 8, 15–18) or fixed-bed (19–23) reactors. Despite the previous successful use of supported catalysts, it is thought that the mass transfer limitation might outweigh the advantages of a fixed catalyst (2). In the case of a photocatalyst fixed on the inner wall of a tube of several millimeters in diameter, mass transfer influence exists, and a clear sign of this is

the dependence of the reaction rate on the flow rate (24, 25). A reactor analysis (26) indicates that the observed rate can be described well by considering both mass transfer and chemical kinetics. Matthews (15) used coiled tube reactors coated with and without TiO₂ to compare performances of slurry and supported catalysts. For most of the solutes tested, the degradation rates of slurries were found higher than those of supported catalysts for influent concentrations of up to 50 mg/L. In another test carried by Turchi and Mehos (27), reactor tubes were inserted with a TiO₂-bonded woven fiberglass fabric or passed with a catalyst slurry. They found that the TCE degradation rate of the slurry was almost twice of that of the supported catalyst.

Because photocatalysis is an extremely complicated process, systematic investigations are required to design and optimize the photoreactors. In this study, supported and slurry catalyst options were individually optimized and compared to each other under identical conditions. Promising catalyst/reactor options were identified and further tested under a variety of operational conditions. The reactor size is reported in empty bed contact time (EBCT) because void fraction and bulk density depend on the type of support. For engineering cost analyses, the required EBCT and the bulk density of the supported catalyst are the most convenient parameters that specify a given reactor design.

Development and Optimization of Supported Photocatalysts. *Control and Dark Experiments.* In one experiment, the reactors were packed with bare supports A, B, C, and E without TiO₂ loading and also with the same supports but loaded with TiO₂. During the 1.5-h exposure to solar irradiation, all the reactors were fed with the same TCE influent concentration of 4 mg/L at a hydraulic loading of 19 m/h. Effluent TCE concentrations of the reactors packed with bare supports gradually increased to more than 95% of the influent, while the effluents of reactors packed with catalyst-loaded supports remained low. In another experiment, reactors were packed with catalyst-loaded supports. After exposure to solar irradiation for 2 h, the photoreactors were wrapped with aluminum foil. Within the following 1.5 h, effluents of all the reactors reached the influent level. These two experiments suggest that the unloaded support material has negligible photoactivity; the catalyst loaded supports have limited adsorption capacities for TCE; and sunlight is required to activate the supported photocatalysts.

Catalyst and Support Type. Figure 3 shows an experiment conducted by using five reactors packed with different catalyst/support options. Support B loaded with 1 wt % platinized TiO₂ shows the fastest degradation kinetics. It is clear that the platinized TiO₂ works better than the non-platinized TiO₂ based on the results from support A. An early study (12) showed that platinized TiO₂ decreased the half-life of TCE by a factor of 5.2 over non-platinized TiO₂ in a batch slurry reactor. Here the platinized TiO₂ on support A gave a reduction factor of 1.8 in the continuous flow fixed-bed reactor.

As seen in Figure 3, TiO₂ on support D does not perform as well as other options. However, the reactor configuration used in this study may not exploit its advantages as has been reported by Al-Ekabi et al. (28). The support E option is not shown in Figure 3 because it was not fully developed at the time the experiment was conducted. Later tests found that for the tube reactor configuration, the glass wool could not be packed in a reproducible fashion.
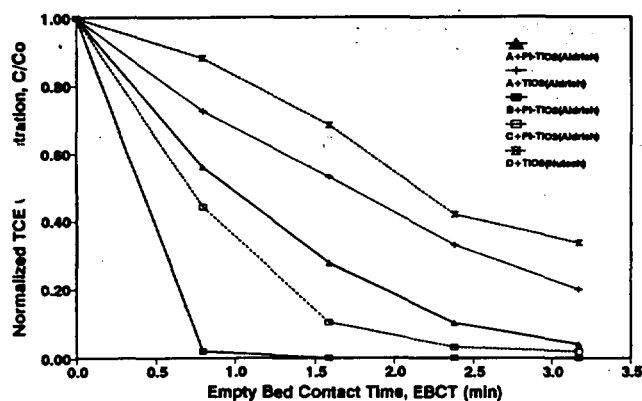
Figure 3. Comparison of TCE degradation for five supported catalyst options. An influent concentration of 250 μg/L was used at a hydraulic loading of 19 m/h. The experiment was conducted at 5:00 P.M., July 11, 1992, with a solar irradiance of 3.16 mW/cm².
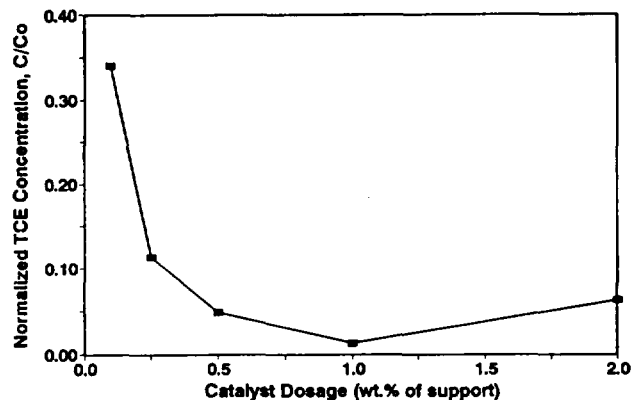
Figure 4. TCE degradation for various dosages of platinized TiO₂ on support B (35 × 60). An influent concentration of 8 mg/L was used at a hydraulic loading of 19 m/h. The data were from the second sample ports at EBCT of 48 s. The experiment was conducted at 5:30 P.M. on September 20, 1992, with a solar irradiance of 1.91 mW/cm².

Thus, it was impossible to optimize this option due to packing and repacking requirements for complete evaluation. Moreover, this option also had a great pressure drop if high hydraulic loading is applied. For support C option, firm catalyst bonding required complex surface cleaning and/or etching procedures. No sign of high degradation kinetics with this option was observed in the first several test runs, probably due to lower specific surface area and less light penetration. Based on these considerations, support C and E options were not further evaluated. On the other side, support A option had relatively fast degradation kinetics, and a low support material cost (virtually only shipping and handling); support B option had high light efficiency and fast degradation kinetics. Both the support options showed application potentials in the preliminary studies. Therefore, support options A and B were further optimized with catalyst dosage, support particle size, and calcination temperature. These two options were also used to study the impacts of other physical and chemical factors on reactor performances.

Catalyst Dosage. Support B option was evaluated with ∩atalyst dosages of 0.1, 0.25, 0.5, 1, 2, 4, and 8 wt %. Figure lisplays TCE concentrations at the second sample ports of reactors for various catalyst dosages. Clearly, the optimal catalyst dosage was 1 wt % as shown in the figure. For support A option, a high degree of degradation was found with catalyst dosages between 1 and 4 wt %. These results suggest that the more UV-light-transmissive sup-
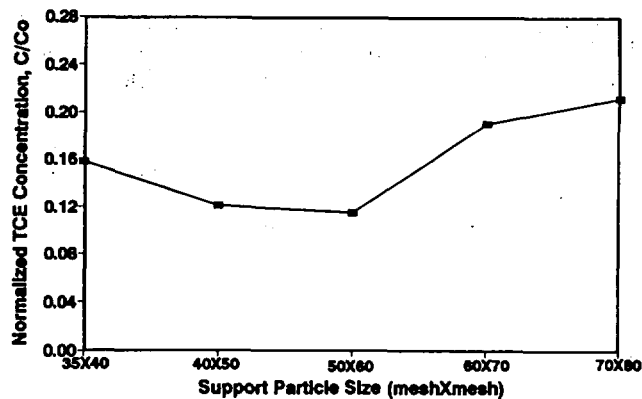
Figure 5. Effect of varying support particle size on TCE degradation for 1 wt % platinized TiO₂ support B (35 × 60). An influent concentration of 13 mg/L was used at a hydraulic loading of 19 m/h. The data were from the second sample ports at EBCT of 48 s. The experiment was conducted at 3:40 P.M. on October 1, 1992, with a solar irradiance of 3.12 mW/cm².
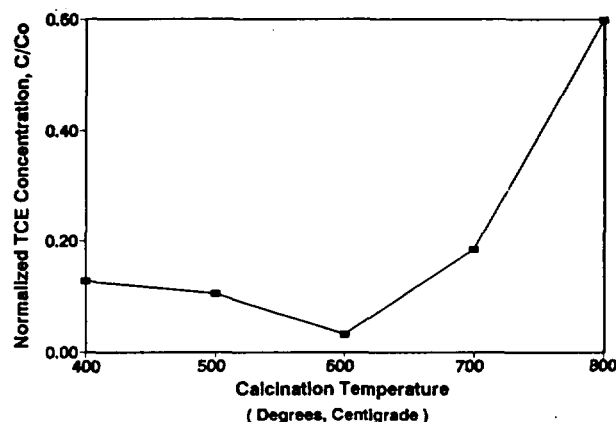
Figure 6. Impact of calcination temperature on TCE degradation for 1 wt % platinized TiO₂ on support B (35 × 60). An influent concentration of 9 mg/L was used at a hydraulic loading of 19 m/h. The data were from the second sample ports at EBCT of 48 s. The experiment conducted at 1:15 P.M. on October 11, 1992, with a solar irradiance of 3.14 mW/cm².

port required less photocatalyst on the support than the less UV-transmissive support in order to achieve the best degradation.

Support Particle Size. The impact of photocatalyst support particle size is shown in Figure 5 for support B option. The optimal particle size appears to be 50 × 60 mesh size; however, about 80% removal of initial TCE was observed over the entire tested range from 35 × 40 to 60 × 70 mesh sizes with an EBCT of 48 s. Larger particles create a lower head loss and, therefore, are favored for reducing operational costs. In the case of support A option, the maximum degradation was found at 20 × 30 mesh size, and this was the largest size tested for that support.

Calcination Temperature. Calcination temperature affects not only the attachment of a catalyst to its support but also the degradation kinetics, as shown in Figure 6. For support B option, the optimal calcination temperature was found to be 600 °C. While for support A, the impact was more critical, and degradation kinetics varied greatly with temperature. The optimal temperature was found at about 500 °C. The existence of the optimal calcination temperature probably is mainly due to catalyst annealing—a TiO₂ crystal with fewer defects has less chance for bulk electron hole recombinations. However, when the temperature is over 600 °C, anatase starts to convert
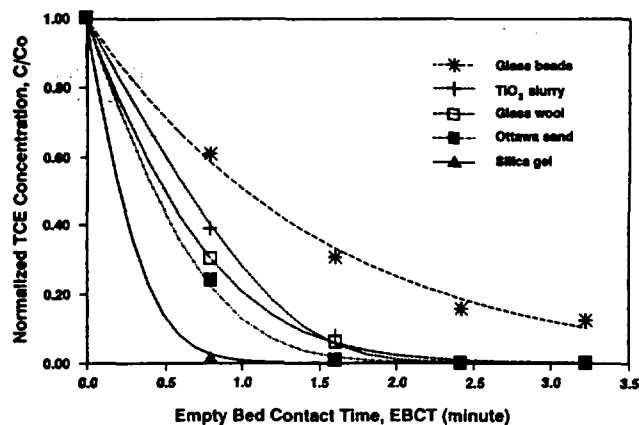
Figure 7. Comparison of optimized support A and support B options to the optimized slurry and other support options. An influent concentration of 10 mg/L was used at a hydraulic loading of 19 m/h for each of the catalyst/reactor options. The experiment was conducted at 3:40 P.M. on September 20, 1992, with a solar irradiance of 2.70 mW/cm². Symbols represent the experimental data, and the lines are the fit curves generated by using the Langmuir–Hinshelwood parameters in Table 2.

to rutile, a less photoactive phase of TiO_2. The different optimal calcination temperatures of options A and B imply a difference in catalyst-support interactions.

Comparison of Optimized Supported and Slurry Photocatalysts. Four reactors with various support options were compared to each other and to an identical reactor through which a slurry was passed with the same flow rate. Support options A and B were optimized as described previously.

The slurry was optimized with respect to preparation method, catalyst type, and catalyst dosage. Three methods for preparing a concentrated slurry were compared to each other: nonsonication, sonication with common laboratory sonicating bath, and sonication with sonic dismenberator. Sonication with sonic dismenberator gave the best degradation results. Two reactors were compared side by side using slurries containing non-platinized and platinized TiO_2. For an EBCT of 48 s, platinized TiO_2 gave 96% degradation of the influent TCE while non-platinized TiO_2 gave about 75%. Further optimization of the slurry with different catalyst dosages was carried out only on the platinized TiO_2 by testing 0.05, 0.1, 0.25, 0.5, and 1 g of platinized TiO_2 for every liter of water. The dosage of 0.25 g/L gave the fastest degradation kinetics.

In this comparison test, the catalyst dosages used were 1 wt % for supports A, B, and C; 10 wt % for support E; and 0.25 g/L for slurry. As shown in Figure 7, support option B gave the fastest degradation. The time required for 90% degradation in terms of EBCT for support options B, E, and A and the slurry are 0.73, 1.28, 1.47, and 1.54 min, respectively. All effluent concentrations of supported options and the slurry were below the detection limit of 0.5 μg/L after 3.2 min of EBCT, except support option C. By improving the preparation method, platinized TiO_2 on support A showed faster degradation than on support C, thus reversing the trend shown in Figure 3.

The Langmuir–Hinshelwood rate expression was used to compare the degradation rates using supported and slurry catalyst reactors:

$$r = -\frac{Kk[\text{TCE}]}{1 + k[\text{TCE}]} \quad (1)$$

K is the rate constant; k is the adsorption constant; and

[TCE] is the concentration of TCE. After substituting this rate expression into a mass balance on a plug flow reactor, the following expression was obtained:

$$\text{EBCT} = \frac{1}{Kk} \ln\left(\frac{[\text{TCE}]_{\text{influent}}}{[\text{TCE}]_{\text{effluent}}}\right) + \frac{1}{K}([\text{TCE}]_{\text{influent}} - [\text{TCE}]_{\text{effluent}}) \quad (2)$$

Two linear forms of eq 2 were used to fit the experimental data, and they are shown as the following:

$$\frac{\text{EBCT}}{\ln\left(\dfrac{[\text{TCE}]_{\text{influent}}}{[\text{TCE}]_{\text{effluent}}}\right)} = \frac{1}{Kk} + \frac{1}{K}\frac{([\text{TCE}]_{\text{influent}} - [\text{TCE}]_{\text{effluent}})}{\ln\left(\dfrac{[\text{TCE}]_{\text{influent}}}{[\text{TCE}]_{\text{effluent}}}\right)} \quad (3)$$

and

$$\frac{\text{EBCT}}{([\text{TCE}]_{\text{influent}} - [\text{TCE}]_{\text{effluent}})} = \frac{1}{K} + \frac{1}{Kk}\frac{\ln\left(\dfrac{[\text{TCE}]_{\text{influent}}}{[\text{TCE}]_{\text{effluent}}}\right)}{([\text{TCE}]_{\text{influent}} - [\text{TCE}]_{\text{effluent}})} \quad (4)$$

The Langmuir–Hinshelwood parameters, K and k, are determined by fitting the experimental data to either eq 3 or eq 4. The obtained values for both the supported and slurry catalysts are reported in Table 2. The comparison between the experimental data and the fit equations is shown in Figure 7. As indicated in Table 2, the degradation rate for the best supported catalyst, support B option, is approximately four times the value that was obtained by using the slurry catalyst.

Impact of Other Physical and Chemical Factors. *Solar Irradiance and Weather Condition.* As expected, TCE degradation increased with increasing solar irradiance. Support A option is sensitive to light intensity as shown in Figure 8. The dependence of degradation kinetics on solar irradiance was examined with diurnal variation of sunlight from early morning to early afternoon. Support B option showed a high light efficiency and fast degradation kinetics. In Figure 9, TCE degradation was observed with very low irradiance in a rainy late afternoon.

In the engineering of photocatalytic reactors, it is convenient to define an apparent quantum yield as

$$\phi_{\lambda_1-\lambda_2} = \frac{\text{mol of organic compound degraded}}{\text{einsteins received by reactor}} \quad (5)$$

"mol of compound degraded" refers to the degradation of a specific organic compound; "einsteins received by reactor" is used because the actual number of photons absorbed by the media is difficult to determine. In fact, the actual number of photons absorbed by the media does not directly relate to the amount of incident solar radiance required for a certain level of degradation. Therefore, an "apparent quantum yield" as defined in eq 5 would be more useful for the design and scaleup of photoreactors and the evaluation of the overall light efficiency of a photocatalytic process. λ_1 is 300 nm, and λ_2 is 387.5 nm in the case of this study that anatase-form TiO_2 and solar irradiation are involved.

The total number of einsteins received by a reactor was determined by measuring and integrating the solar irra-

Table 2. Langmuir–Hinshelwood Parameters of TCE Degradation with Supported and Slurry TiO₂

support or slurry	K (mg/L·min)	k (L/mg)	R^2	reaction rate (mg/L·min) (at influent of 10 mg/L)
silica gel (support B)	49.46	0.13	0.9640[a]	27.56
Ottawa sand (support A)	20.24	0.18	0.9840[a]	13.04
glass wool (support E)	23.78	0.10	0.9015[a]	12.03
TiO₂ slurry	8.20	0.55	0.9849[b]	6.93
glass beads (support D)	48.54	0.02	0.8659[a]	6.66

[a] Linear regression conducted with eq 3. [b] Linear regression conducted with eq 4.
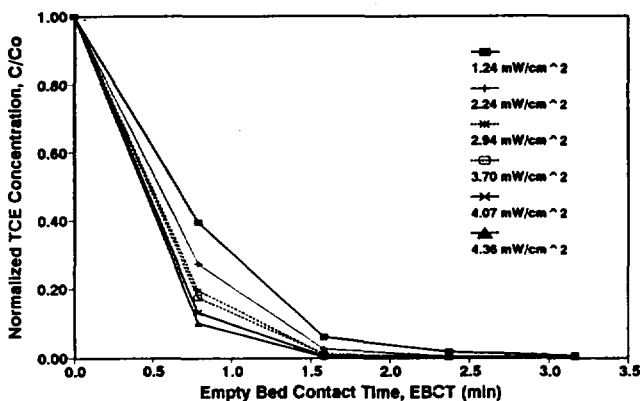
Figure 8. Impact of solar irradiance on TCE degradation for 1 wt % platinized TiO₂ on support A (30 × 40). An influent concentration of 2 mg/L was used at a hydraulic loading of 19 m/h. The experiment was conducted on July 29, 1992, from 8:30 A.M. to 2:00 P.M.

Figure 10. Impact of influent concentration on TCE degradation for 1 wt % platinized TiO₂ on support B (35 × 60). The hydraulic loading was 19 m/h. The experiment was conducted at 2:20 P.M. on September 8, 1992, with a solar irradiance of 3.80 mW/cm².

Figure 9. TCE degradation on a rainy day in the fall of 1992 with 1 wt % platinized TiO₂ on support B (35 × 60). An influent concentration of 8.5 mg/L was used at a hydraulic loading of 19 m/h. The experiments were conducted on July 29, 1992, at 1:30 P.M. and 5:00 P.M. with a solar irradiance of 0.16 and 0.07 mW/cm², respectively.

Figure 11. Impact of influent pH on TCE degradation for 1 wt % platinized TiO₂ on support B (35 × 60). An influent concentration of 7 mg/L was used at a hydraulic loading of 19 m/h. The data were from the second sample ports at EBCT of 48 s. The experiment was conducted at 3:30 P.M. on September 8, 1992, with a solar irradiance of 3.81 mW/cm².

diance (every 45°) around the reactor tube. For support A, based on the data shown in Figure 8, the apparent quantum yield varies as $I^{-0.65}$; I is solar irradiance. The apparent quantum yields were 0.50%, 0.34%, 0.29%, 0.24%, 0.23%, and 0.22%, corresponding to the increasing solar irradiance values shown in the figure, respectively. In light rain in the late afternoon with irradiance of 0.07 mW/cm², support B option achieved virtually complete degradation as the data suggested in Figure 9, resulting in an apparent quantum yield of 40%. For this support option, the apparent quantum yield varies as I^{-1} over the range of 1–5 mW/cm² (sunny days). Uncontrollable weather conditions prevented determining the apparent quantum yield dependence on I at low light intensities (overcast and rainy days) in this study.

Influent Concentration and Dissolved Oxygen. In Figure 10, high percent TCE degradation is shown up to an influent concentration of 38 mg/L; still, more than 95%

of the 54 mg/L influent concentration was destroyed in approximately 3 min of EBCT. A typical initial DO in the aqueous solution for this study was 8.5 mg/L; if this is assumed to be the only electron acceptor available, the DO would be exhausted to mineralize TCE concentrations greater than 23.3 mg/L. The insufficient DO for higher influent concentrations is likely the reason for the dramatic decrease of percent degradation in these cases. For a given EBCT, the percent degradation increased with decreasing influent concentrations.

pH Effects. The impact of pH on degradation with support B option is displayed in Figure 11. Although the optimal pH shows at 5, good degradation is observed over a wide range of pH values (3–7) and an EBCT as short as 48 s. Nearly 99.9% degradation was obtained after an EBCT of 2.4 min for a pH of 10.5. In contrast, substantial impact of pH was found on the slurry operation and it is
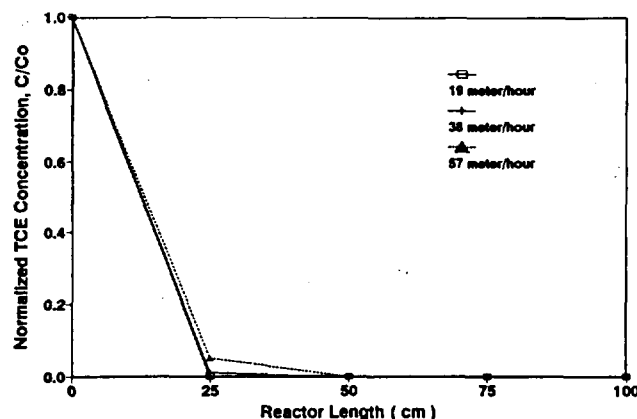
Figure 12. Influence of hydraulic loading on TCE degradation for 1 wt % platinized TiO₂ on support B (35 × 60). The influent concentration was 1.2 mg/L, and the experiment was conducted at 12:30 P.M. on August 10, 1992, with a solar irradiance of 4.63 mW/cm².
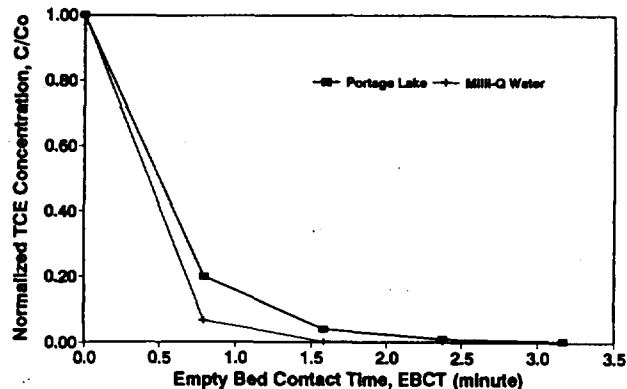

Figure 13. Impact of BNOM on TCE degradation for 1 wt % platinized TiO₂ on support B (35 × 60). An influent TCE concentration of 12 mg/L was used at a hydraulic loading of 19 m/h. The NPOC of the surface water was about 2 mg/L. The experiment was conducted at 5:10 P.M. on October 5, 1992, with a solar irradiance of 1.73 mW/cm².

thought to be caused by flocculation of the TiO₂ particles. For example at a pH = 3, TiO₂ particles flocculated and less than half (47%) influent 2.3 mg/L TCE was degraded. It appears this problem can be avoided when the photocatalyst is fixed on a support.

Hydraulic Loading (Flow Rate). For support B option, hydraulic loading does not have a significant impact on the reactor performance as shown in Figure 12.

Calculations were made to assess the role of mass transfer. At a given hydraulic loading, the TCE film transfer coefficient, k_f, for a spherical support was evaluated by using the Gnielinski correlation of the following form:

$$Sh = (2 + 0.644Re^{1/2}Sc^{1/3})[1 + 1.5(1 - \epsilon_B)] = \frac{k_f d_p}{D_L} \quad (6)$$

Here Sh is Sherwood number, Re is Reynolds number, Sc is Schmidt number, ϵ_B is bed porosity, and D_L is diffusivity of TCE in water. Assuming the entire surface of a support is photoactive and the surface reaction rate is infinite, the EBCT using a plug flow reactor for a given percent degradation of x can be obtained as

$$EBCT = -\frac{\ln(1-x)}{k_f S_V} \quad (7)$$

where S_V is the area available for mass transfer per volume of a reactor bed. At a hydraulic loading of 57 m/h and a desired degradation of 95%, the calculated length of mass transfer zone is 0.07 m for support B option. This is much shorter than the 0.25-m reactor length as shown in Figure 12. Based on this preliminary analysis, TCE degradation with supported catalysts may not be mass transfer limited.

Although mass transfer does not limit the degradation rate, its impact can be evaluated by determining the effectiveness factor. In this case, the effectiveness factor may be defined as the ratio of the actual degradation rate to the rate that would result if the entire external surface of the supported catalyst were exposed to the bulk TCE concentration. For the experimental data shown in Figure 12, the effectiveness factor was estimated to be about 90%. This result implies that the impact of mass transfer may be ignored because the degradation rate was only 10% slower due to mass transfer.

The above calculations for both the mass transfer zone length and the effectiveness factor did not include the enhancement of mass transfer due to OH/TCE reaction in the diffusion boundary layer surrounding the catalyst.
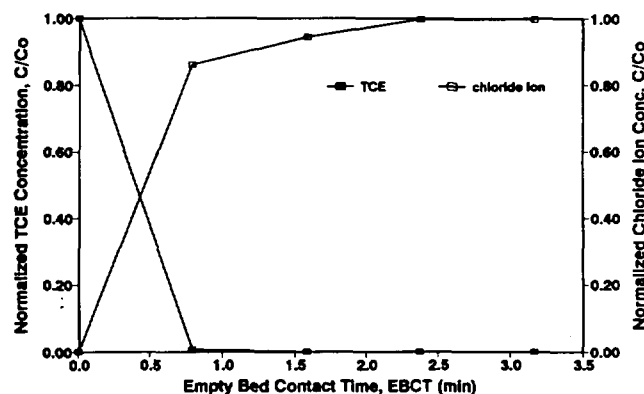
Figure 14. Comparison of TCE degradation to the appearance of chloride ion for 4 wt % platinized TiO₂ on support B (35 × 60). An influent concentration of 2.4 mg/L was used at a hydraulic loading of 19 m/h. The experiment was conducted at 11:30 A.M. on August 13, 1992, with a solar irradiance of 3.92 mW/cm².

If the enhancement is considered, one may expect the length of the mass transfer zone to be shorter and the effectiveness factor to be closer to unity.

Water Matrix. Two reactors were operated in parallel to evaluate the impact of BNOM: one was fed with Milli-Q water; the other was fed with the surface water—both were spiked to the same TCE concentration. As shown in Figure 13, there is only a slight decrease in the degradation rate with the surface water matrix. This result suggests that low levels of BNOM may not have a significant impact on organic degradation in this process. In addition, approximately 25% of the influent NPOC (about 2 mg/L) was mineralized within 3.2 min of EBCT.

Photocatalyst Attrition, Degradation, and Fouling. In a continuous test using Milli-Q water and support B option, there was no visible catalyst attrition after 1 h of operation and no noticeable photoactivity decrease at the end of the 20-day run. From another 10-day experiment, no significant activity loss was observed with the surface water. Although these results demonstrate that the photoactivities of supported catalysts may be retained for short periods of time with deionized water and low BNOM surface water, field trials of longer duration are required for further evaluation.

Complete Mineralization. The causes for TCE disappearance include formation of intermediates or byproducts, adsorption onto the catalyst/support, and mineralization. Continuous flow tests in the dark and adsorption isotherms ruled out adsorption as one of the removal

mechanisms. Figure 14 displays the normalized TCE degradation and the chloride ion (Cl⁻) production as compared to that which is expected if all the TCE is completely mineralized. Although the chloride ion emergence lags behind the TCE disappearance, all the chlorinated intermediates were destroyed within 3.2 min of EBCT. Chloride ion production is affected by influent concentration and solar irradiance. In one experiment conducted in light rain with influent TCE concentration of 12.5 mg/L, though more than 95% of the TCE was degraded, the chloride ion production was only 70% according to stoichiometry. However, all the TCE and intermediates could have been mineralized if a longer reactor was used.

Summaries and Conclusions

Highly active supported photocatalysts were developed, and promising options were identified and further optimized. Greater degradation was observed using TiO_2 on three silica-based supports than was observed in a slurry. The degradation rate obtained by using support B option is approximately four times that obtained by using a TiO_2 slurry. The most active catalyst identified in the batch slurry screening tests also had the fastest degradation rate when it was fixed on a support. These observations and preliminary analyses suggested that mass transfer and light penetration may not limit degradation rate in a fixed-bed photoreactor. Consequently, research and development of more photoactive catalysts will still lead to the improvement of reactor performance.

Solar irradiation is capable of mineralizing TCE under a wide range of weather conditions with various irradiance. Rainy late afternoon experiments conducted in the fall exhibited efficient TCE degradation. Apparent quantum yields as high as 40% were observed by using a supported photocatalyst. It has been proven that solar irradiation can be used as a reliable UV source for the engineering of photocatalysis.

The photocatalysts supported on silica-based material were able to degrade TCE over a wide range of influent concentrations, pH values, and hydraulic loadings. DO is a sufficient electron acceptor.

A 20-day test with Milli-Q water showed no noticeable decrease in photoactivity of a supported catalyst. Although the BNOM of a surface water slowed the TCE degradation rate, it was not significant and a 10-day test showed no appreciable further decrease. Long-term tests are required for potential real-world applications.

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TECHNICAL NOTE

The Synthesis, Characterization, and Testing of a Reagent for the Selective Removal of Dichromate and Perchlorate from Aqueous Solution

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ABSTRACT

N-4-Vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane was synthesized and tested to determine its ability to selectively precipitate anions. Fifty-one common anions were tested. The reagent reacted only with nine: dichromate, dithionate, ferricyanide, tetrafluoroborate, iodide, nitroferricyanide, perchlorate, persulfate, and picrate.

INTRODUCTION

A serendipitous discovery was made when the preparation of a reagent to selectively remove phosphate from water was undertaken. While N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane does not precipitate phosphate, it does selectively remove dichromate and perchlorate from aqueous solution. Cr(VI) has been found to be harmful to the human population as well as the environment. It has been found to be toxic to aquatic life forms (1) and to be a carcinogen and mutagen (2, 3). A reagent which can separate dichromate from waste streams would be extremely beneficial. The removal of perchlorate from the laboratory environment would also be very useful when procedures employing perchloric acid are done. Pure $HClO_4$ is a colorless mobile, shock-sensitive liquid, while the anhydrous form is an extremely powerful oxidizing agent which reacts explosively with most organic materials (4). Figure 1 shows the structure of the compound prepared, characterized, and tested.
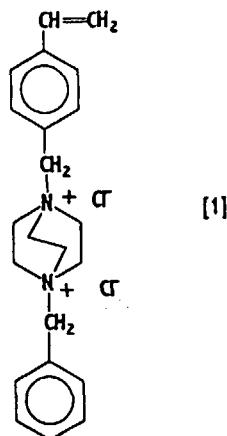
FIG. 1 Compound synthesized and tested: N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.

EXPERIMENTAL

All reagents used in testing were reagent grade and used as received. Solutions were prepared from the following: lithium fluoride, picric acid, and stannous titanate; potassium or sodium salts of acetate, aluminate, arsenate, arsenite, bicarbonate, bismuthate, bisulfate, bisulfite, borate, bromate, bromide, carbonate, chlorate, chloride, chromate, citrate, cyanate, cyanide, dichromate, dithionate, dithionite, ferricyanide, ferrocyanide, tetrafluoroborate, hydroxide, iodate, iodide, metaborate, molybdate, nitrate, nitrite, nitroferricyanide, oxalate, perchlorate, periodate, persulfate, selenate, selenite, silicate, sulfate, sulfite, thiocyanate, thiosul-
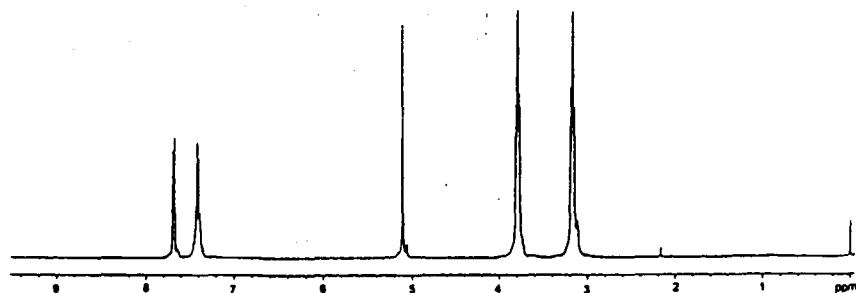
FIG. 2   NMR spectrum of N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride in CDCl₃.

fate, tungstate, vanadate, tribasic phosphate, dibasic phosphate, and monobasic phosphate. All water was distilled and deionized.

The synthesized compounds were characterized with a Varian 400 MHz NMR Spectrometer, Hewlett-Packard model 5859A Mass Spectrometer, and a Perkin-Elmer model 1310 IR Spectrometer. All melting points were obtained without correction using a Fisher–Johns melting point apparatus. Elemental Analyses were done at Galbraith Laboratories, Knoxville, TN 37950-1610.

Synthetic Procedures

Preparation of N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride was achieved via a nucleophilic substitution reaction. To a 500-mL beaker, equipped with a magnetic stir bar, was added 33.65 g (0.30 mol) of diazabicyclo[2.2.2]octane and 37.98 g (0.30 mol) of benzyl chloride to 300 mL acetone. After 5 seconds the white crystalline precipitate of the product
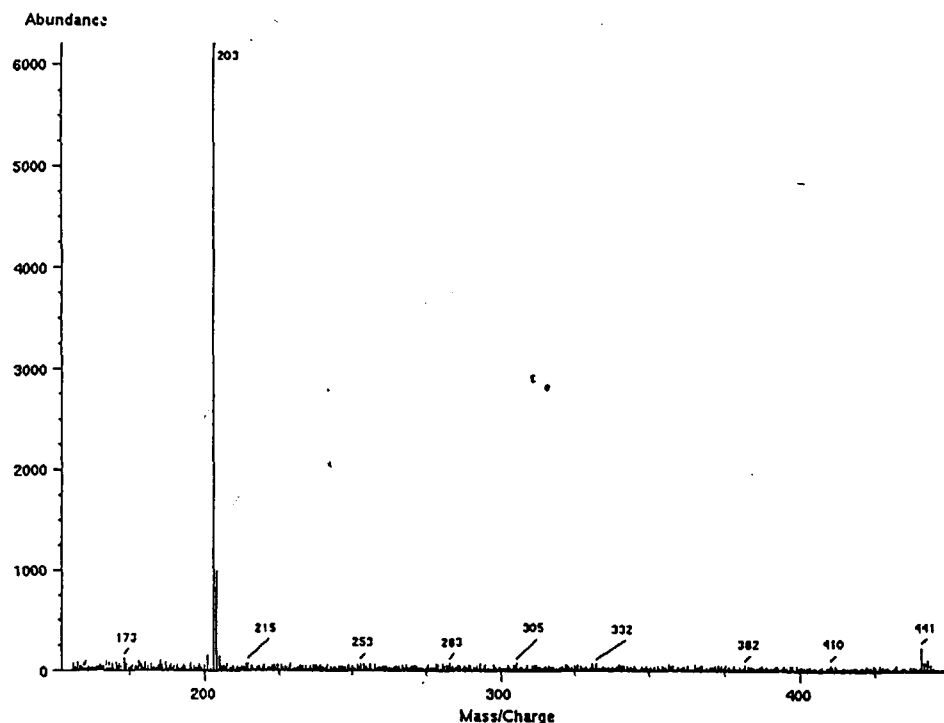
FIG. 3   MS (fast atom bombardment ionization) of N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride.

was collected crystallized two times from acetone, and dried under vacuum. 61.54 g (85.91% yield) of N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride was obtained with a melting point of 150°C (hardens at 166°C). NMR (Fig. 2): 3.2 ppm: (N—CH$_2$—), 3.8 ppm: (N$^+$—CH$_2$—), 7.4 and 7.7 ppm: (aromatic). MS (Fig. 3): 203 (M$^+$—Cl). IR (Fig. 4).

Preparation of N-4-vinylbenzyl-N'-benzyl'-1,4-diazabicyclo[2.2.2]octane dichloride was also achieved via a nucleophilic substitution reaction. To a 250-mL 3-necked round bottom flask, equipped with a thermometer, magnetic stir bar, water condenser, and nitrogen atmosphere, was added 4.92 g (0.013 mol) N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride and 1.92 g (0.013 mol) p-vinylbenzyl chloride to 125 mL chloroform. The temperature was maintained at 57°C for 22 hours. The white precipitate was recrystallized from chloroform and then dissolved in methanol, filtered, and dried under vacuum. 3.73 g (75.55% yield) of N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride was obtained with a melting point of 200°C (decomposes to light yellow), 247°C (dark yellow). Elemental analysis: 64.62% C, 7.52% H, 6.71% N, 17.71% Cl. Theoretical: 67.5% C, 7.2% H, 7.2% N, 17.9% Cl. NMR (Fig. 5): 3.9 ppm (—N$^+$—CH$_2$—CH$_2$—N$^+$—), 4.95 ppm (CH$_2$), 5.39 and 5.95 ppm (CH$_2$=), 6.8 ppm (CH=), 7.4–7.65 ppm (aromatic). MS (Fig. 6): 355 (M$^+$—Cl). IR (Fig. 7).
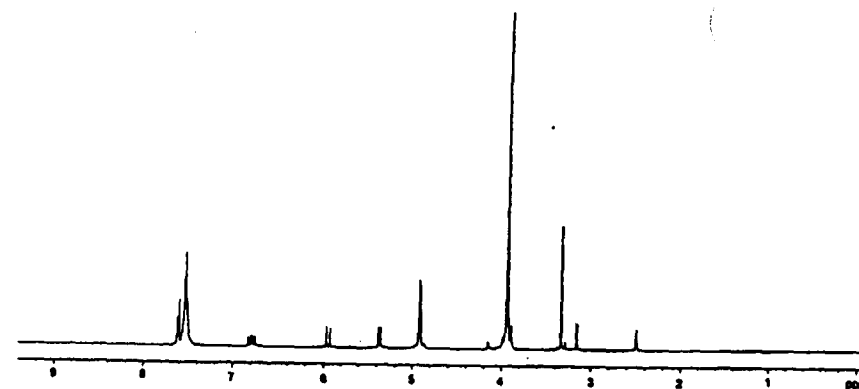
FIG. 5 NMR spectrum of N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride in DMSO.

FIG. 4 IR spectrum of N-benzyl-1,4-diazabicyclo[2.2.2]octane chloride.
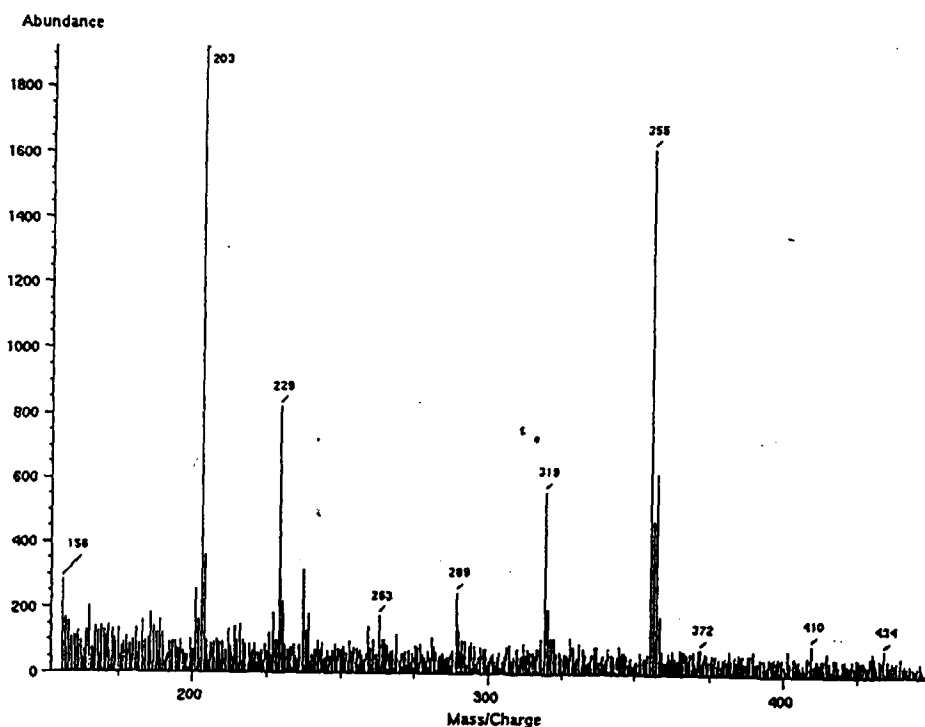
FIG. 6 MS (fast atom bombardment ionization) of N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.
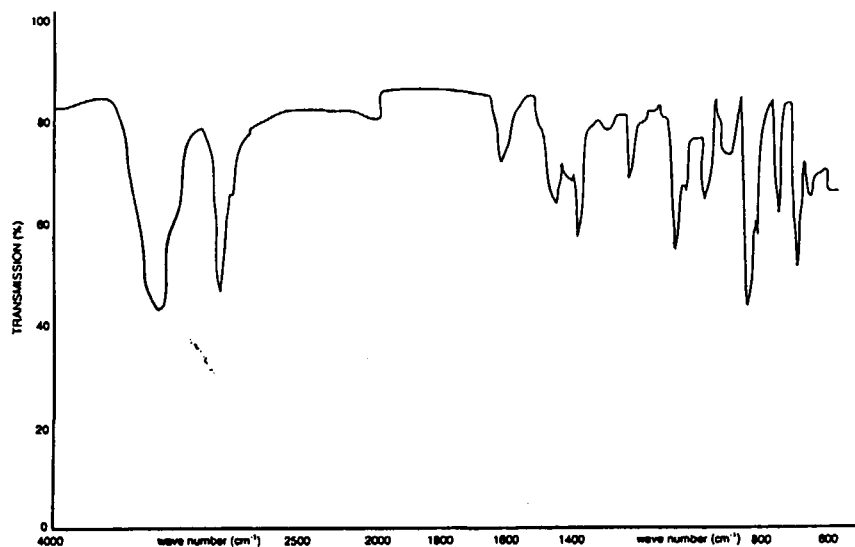
FIG. 7   IR spectrum of N-4-vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.

Analytical Tests

A 0.100 M solution of [1] was prepared by dissolving 3.918 g in 100 mL water. A solution (0.1 M) of each anion was prepared. An anion solution (10 mL) was placed in a test tube, and the reagent solution (2 mL) added. Observations were made immediately on any reactions and again at 2 and 24 hours.

RESULTS AND DISCUSSION

The results of the reactions between the reagent and the anions are summarized in Table 1. Fifty-one anions were tested. In general, one of three results were observed: no reaction, immediate precipitation, precipitation at 2 hours. In general, the precipitates were white, crystalline, and easy to filter and recover.

TABLE 1
Anion Tests with N-4-Vinylbenzyl-N'-benzyl-1,4-diazabicyclo[2.2.2]octane Dichloride

	No Reaction	
Acetate	Chromate	Periodate
Aluminate	Citrate	Selenate
Arsenate	Cyanate	Selenite
Arsenite	Cyanide	Silicate
Bicarbonate	Dithionite	Sulfate
Bismuthate	Ferrocyanide	Sulfite
Bisulfate	Fluoride	Thiocyanate
Bisulfite	Hydroxide	Thiosulfate
Borate	Iodate	Titanate
Bromate	Metaborate	Tungstate
Bromide	Molybdate	Vanadate
Carbonate	Nitrate	Tribasic Phosphate
Chlorate	Nitrite	Dibasic Phosphate
Cloride	Oxalate	Monobasic Phosphate

Formation of an Immediate Precipitate

Dichromate
Ferricyanide
Nitroferricyanide
Perchlorate
Persulfate
Picrate

Formation of a Precipitate at 2 Hours

Dithionate
Tetrafluoroborate
Iodide

CONCLUSIONS

1. The reagent under investigation, [1], is selective toward a limited number of anions: dichromate, dithionate, ferricyanide, tetrafluoroborate, iodide, nitroferricyanide, perchlorate, persulfate, and picrate.
2. The selected anions are generally large and either multivalent or easily polarized.
3. Generally those anions which were going to react did so quickly.

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